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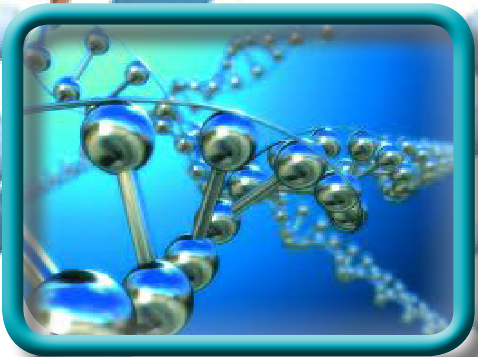

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Review on Synthesis and Applications of Nickel Nanoparticles

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Abstract

Now-a-days nickel nanoparticles (Ni NPs) are gaining attention due to its improved electrical, magnetic and catalytic properties. Currently, Ni NPs are synthesized by chemical reduction, hydrothermal, microemulsion and microwave assisted synthesis methods. In all these methods all researchers have tried to tune the size of Ni NPs, since the electrical, magnetic properties and catalytic activity increase with decreasing size of Ni NPs. The preparation of Ni NPs in large amounts is possible using the reported methods. New methods for synthesis are needed to avoid usage of toxic reducing and stabilizing agents in preparing Ni NPs at industrial scale.

Key Words : Ni Nps, Toxic Reducing Agent, Stabilizing Agent, Chemoselective.

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INTRODUCTION

Nanotechnology is considered to be as one of the vast and fast developing fields in science. The term "nanotech" itself represents that most of the technology can be used for manipulating the matter on atomic and molecular scale. This field was getting more popularity in the recent periods of times because most of the researchers are paying their keen interest towards this nanotechnological field and they are also more enthusiastic to manipulate the matter in nanoscale and developing or creating new properties within these materials which are used as functionalized materials to the present society. Nanotechnology is very diverse in nature; it starts its extending character by applying new methodologies for building up a completely new material or device with appropriate dimensions in nanoscale level. Furthermore, the scientists are continuously investigating the properties of those synthesized materials whether they can be used directly or some modifications have to be carried out to control the properties in the atomic scale level. The highlight property which we can observe in nanomaterials, is molecular self-assembly capacity. Nanomaterials in the modern era are classified into two major groups, namely natural nanomaterials and synthetic nanomaterials. The common examples for naturally occurring nanomaterials are milk, blood, cotton, paper, etc, whereas the synthetic nanomaterials include NPs. These NPs or nanocrystals are made from the metal and metal oxide precursors and possess many of the intrinsic properties within them such as mechanical, electrical, magnetic, optical, and chemical. These properties mainly depend upon their size and shape, but these materials further can be finely tuned for developing desirable properties within them by controlling size and shape of the particles.

By taking the advantages of manipulation of bulk material to nanomaterials many researchers have developed several synthesis procedures for noble metal NPs such as Ag, Au, Pt, Pd, Ir, Os, Rh, and Ru, transition metal NPs such as Fe, Ni, Co and Cu. Synthesis of transition metal NPs have been studied more, because of various applications such as electronic, magnetic (1-2), catalysis (10) and various biological applications such as cancer diagnosis, drug delivery, hyperthermia, cell and protein separation (3-5), and biosensing (6). The produced nickel nanopowders have been used in cellular phones and mobile computers as multilayer supercapacitors (7). Synthesis of Ni NPs in zero valent state is very difficult because its undergoes oxidation very easily when exposed to air leads to the formation of nickel oxide and nickel hydroxides (8).Various procedures have been developed for the synthesis of Ni NPs and few of them are chemical reduction, hydrothermal, microwave assisted synthesis and microemulsion. Among these methods much research has been done on chemical reduction method.

Chemical reduction method

Hu *et. al.,* reported the Ag catalysed synthesis of nickel nanoparticles in ethylene glycol (EG) solution at room temperature (9). The reduction of organometallic salts is done by a reducing agent which initiates the reduction of metal ions and that behaves as seed crystal in situ and acts as a catalyst. The totting up of Ag seeds leads to nucleation and formation of small particles with lower dispersity. The author studied the changes in NPs size by changing the molar ratios of Ni/Ag from 5 to 100 and concluded that the particle size increases from 43.3 nm to 91.4 nm with increasing availability of nickel to Ag seeds. Also the authors studied the effect of temperature on Ag seed size and found that as the temperature increase the seed size decreases, decreased Ag seed triggers the reduction of nickel ions (9). Wang *et. al.,* reported the synthesis of Ni NPs with dissimilar sizes and dissimilar crystal structures with hydrazine hydrate using as reducing agent in the presence of organic modifiers with various functional groups such as citric acid, sodium dodecyl sulphate, Tween 80, PEG 6000, and D-sorbitol in ethanol solution at pH 12 and 80°C and studied the catalytic activity of Ni NPs towards hydrogenation of p-nitrophenol to p-aminophenol. The author proved that the catalytic activity decreased with an increasing in particle size and followed an order of citric acid (9nm), sodium dodecyl sulphate (60nm), Tween 80 (178nm), D-sorbitol (339nm). All the synthesized NPs showed the superior selectivity and catalytic activity than Raney Ni catalyst in the hydrogenation of p-nitrophenol to p-aminophenol (10).

Singla *et. al.,* reported the heterogeneous synthesis of Ni NPs with Pt seed as nucleation initiator followed by growth in aqueous medium using hydrazine hydrate as reducing agent and cationic surfactants such as Cetyl trimethylammonium bromide (CTAB) and lower alkylammoniumbromide mixture of tetraethylammoniumbromide (TEAB) and tetrabutylammoniumbromide (TBAB) at pH 10-12. The size of the nanoparticles was 16 nm with spherical shape and stable for more than 90 days. The transformation of p-nitro phenol to p-nitro amine was carried out at different temperatures; catalytic activity was increased with increase in temperature in the presence of catalyst using hydrazine hydrate as a reducing agent. The author concluded that the catalyst was reused for several times for similar reduction process without losing its catalytic activity (11). Maringa *et. al.,* reported the synthesis of uncapped Ni NPs in ethylene glycol using sodium borohydride as a reducing agent at about 150°C. The electrocatalysis ability of Ni NPs was studied by comparing with nickel phthalocyanine. The modified glassy carbon electrode with Ni NPs performed better in the oxidation of amitrole compared to nickel phthalocyanine modified glassy carbon electrode and bare glassy carbon electrode (12).

Khanna *et. al.,* reported the synthesis of Ni NPs in aqueous medium using succinate as surfactant and sodium formaldehyde sulfoxylate (SFS)/$NaBH_4$ as reducing agent. The authors assumed that succinate ion was first created around Ni^{2+} ions which were slowly converted to metallic NPs via reduction process. Use of $NaBH_4$ leads to straight formation of amorphous NPs without allowing much opportunity to cap the NPs but mild reducing agent SFS can control the nucleation as well as reduction of metal ions thus inhibits surface oxidation during the reaction, leads to formation of crystalline NPs. The author concluded that SFS not only acts as a reducing agent but also a secondary surfactant (13).

Vaseem *et. al.,* reported synthesis of Ni NPs in aqueous medium using glucose as a reducing and capping agent and inactivated the metal surface in the presence of ammonia and the size of the NPs was found to be 3-5nm with ferromagnetic properties (14). Hemalatha *et. al.,* reported the synthesis of Ni NPs using hydrazine hydrate as reducing agent in ethylene glycol solution in the presence of NaOH. The author stated that the presence of NaOH causes release of nitrogen gas during the synthesis leads to an oxygen free environment and hence only bare Ni NPs was obtained in pure form with crystalline form (~ 23.64 nm to 18.63 nm) with face centered cubic (FCC) structure (15). Roselina *et. al.,* synthesized Ni NPs by modified polyol method using hydrazine hydrate and ethylene glycol with different molar ratios(N_2H_4/Ni^{2+}) at a regulatory pH conditions adjusted by NaOH. As the molar ratio (N_2H_4/Ni^{2+}) increased, the rate of a reaction also increased, as well as degree of agglomeration also increased. The TEM analysis showed that particle size ranges between 2 nm to 600 nm (16). Khurana *et. al.,* reported the reduction of nickel salt with $NaBH_4$ in the presence of PEG-4000 (Poly Ethylene Glycol) in ethylene glycol solution lead to the development of mono disperse Ni NPs. TEM studies revealed the size of the nanoparticles was 8nm. The obtained Ni NPs were used as a catalyst in the chemoselective reaction of aromatic aldehydes with Meldrum's acid by Knovenagel condensation to form enol lactone derivatives of active methylene compounds via tandem enol lactonization (17). Alonso *et. al.,* synthesized Ni NPs using lithium as reducing agent in the existence of catalytic quantity of DTBB (4, 40-di-tert-butylbiphenyl) in dry THF under argon atmosphere in room temperature which was utilized in the carbonyl compounds hydrogenation in isopropanol. The synthesised Ni NPs have been found to be finer than commercially obtainable Raney Ni catalyst (18). Couto *et. al.,* studied magnetic properties of Ni NPs synthesized by the reduction of Ni-salts using $NaBH_4$ as a reducing agent and Poly(N-vinylpyrrolidone) (PVP) as a protecting agent. The role of PVP was to arrest aggregation. The size of the nanoparticles was about 3.8 nm with face-centered cubic structure. The materialization of dipolar magnetic couplings among particles caused by small interparticle spacing leads to non-ideal super magnetism of Ni NPs (19).

Wu *et. al.,* successfully prepared Ni NPs by hydrazine hydrate without any protective agent and size of the NPs was about 12nm. From XPS analysis the author revealed that few Ni atoms on Ni NPs chemically react with oxygen and water to form oxides and hydroxides of Ni, which lead to pseudo capacitive capacitance of Ni NPs which was characterised by cyclic voltammetry and galvanostatic testing. The specific capacitance reached up to 416.6F g^{-1} at the current density of 1 A g^{-1} in 1M KOH electrolyte, which is higher than the most carbon electrode materials. The author concluded that the specific capacitance could be further increased by decreasing the size of the Ni NPs (20). Sencanl *et. al.,* synthesised highly dispersed Ni NPs using hydrazine borane as reducing agent and Poly(4-styrenesulfonic acid-c-maleic acid)(PSSMA) as a stabilizing agent with an average size of 8.3nm. The author stated that the release of hydrogen from hydrazine borane reveals the formation kinetics of Ni NPs and PSSMA stabilized Ni NPs were found to be extremely dynamic catalysts in the reaction liberating 2.6-3.0 mol H_2 per mol of hydrazine borane. The hydrogen liberation is a first order kinetics and concluded that it depends upon the concentration of nickel (21). Hou *et. al.,* synthesised Ni NPs using sodium borohydride in the presence of capping agents such as hexadecylamine (HDA) and trioctylphosphine oxide (TOPO). By changing the molar ratios of HAD and TOPO size of the nanoparticles can be turned from 3 to 11nm.The author stated that the capping agents permit the particles to be dissolved in non-polar solvent and also stop agglomeration and oxidation of the particles. Finally the author concluded that as the concentrations of HAD increase the nanocrystalline size decrease (22). Wu *et. al.,* reported synthesis of Ni NPs without protective polymer in ethylene glycol solution using hydrazinium hydroxide and NaOH at a reaction temperature of 60°C for 1h. Here hydrazinium hydroxide acts as a reducing agent and NaOH acts as a catalyst in the formation of Ni NPs. The increase in concentration of hydrazine hydroxide leads to decrease in size of NPs because hydrazine hydroxide increases the faster nucleation and growth of the NPs and N_2 gas evolved during the synthesis and helps in maintaining the inert atmosphere. The size of the NPs was about 9.2nm and the OH groups in ethylene glycol interacts with the surface layer of Ni and acts as a protective layer to inhibit the particle agglomeration. The magnetic capacity signified its super paramagnetic with a saturation magnetization of 22emu/g, a reminant magnetization of 6.4 emu/g and a coercitivity of 0.1 and Oe at a mean diameter of 9.2nm. Due to decrease in thermal energy as the temperature decreases magnetization increases (23).

Ramirez-Meneses *et. al.,* reported the synthesis of Ni NPs using hydroxyl ethyl cellulose (HEC) as a capping agent and hydrazine hydrate as a reducing agent in the presence of NaOH in ethanol solution. The author observed the changes in size of NPs by changing the concentration of HEC and the mean size of the NPs was about 7-13nm.The good electro catalytic activity is shown by Ni NPs with a hydrazine concentration of 1.4 M (24). Chen *et. al.,* synthesized Ni NPs in ethanol using hydrazonium hydroxide as reducing agent and controlled the aggregation, radius and dispersibility by dodecanethiol as the stabilizer (25). The author concluded that the dodecanethiol was successful in regulating the size, aggregation and recuperating the dispersibility of NPs (25). Bai *et. al.,* reported the uniform sized Ni NPs with good dispersion in ethanol through tailored hydrazine reduction without any capping or surfactant in pH regulatory conditions using NaOH. The author concluded that hydrazine is not sufficient to reduce metal ions and ethanol also participated in reduction process after 180°C for complete the reduction process and obtained NPs had smooth surface and size was about 50 nm with a face centered cubic structure (26).

Microwave Assisted Synthesis

Xu *et. al.,* reported the self assembled nickel nanoflowers using hydrazine hydrate as reducing agent and Poly(N-vinylpyrrolidone) (PVP) as stabilizing agent with regulatory amounts of NaOH in the presence of ethylene glycol solution beneath microwave irradiation. Na_2CO_3 played an important role for the formation of monomorphic and uniform Ni NPs. The smaller diameter and a narrow size distribution of nickel nanoflowers are because of tiny amount of NaOH and high amount of hydrazine hydrate. The TEM and XRD measurements manifested the size of the nanoflowers was in the rage of 50-100nm and individual average size of each nanoparticle in Ni nanoflower was about 6.3nm (27). Eluri *et. al.,* reported the nanoflowers and individual Ni NPs by changing the concentrations of NaOH under microwave irradiation with the help of sodium hypophosphate monohydrate as a reducing agent and CTAB (cetyltrimethylammoniumbromide) and PVP (polyvinylpyrolidone) as stabilizing agents. By changing the molar ratios of $[Ni^{+2}]/[NaPH_2O_2]/[NaOH]$ pure and crystalline Ni NPs with a size of 3.9 ± 0.8 to 7.2 ±1.5 nm are prepared. The author concluded that the stabilizing agents (PVP & CTAB) with an open structure did not assist in reducing the size of Ni NPs (28). Motuzas *et. al.,* synthesized ethylene glycol mediated Ni NPs without using any additives in the presence of microwave irradiation. In the presence of microwave irradiation nickel hydroxide precursor gives Ni(II) ions and hydroxyl ions; these hydroxyl ions in turn react with ethylene glycol, where ethylene glycol gets oxidized and releases two electrons; these two electrons involves in reduction of Ni(II) ion to Ni(0) NPs. The author concluded that the process is self-sustainable and formed metallic Ni NPs involves in further oxidation of ethylene glycol, leads to availability of electrons to reduce the Ni precursor in more amounts and in less time.TEM and SEM analysis revealed that there are two batches, larger nanoparticles size ranges from 50-70 nm and smaller nanoparticles size is about 20 nm (29).

Microemulsion method

Using microemulsion of water/CTAB/n-hexanolat at 73°C Chen *et. al.,* synthesized Ni NPs with a face centered cubic structure using hydrazine hydrate as reducing agent (30). The author found that the size of Ni NPs depends on the composition of microemulsion instead of droplet size of the microemulsion; smaller size of NPs could be achieved by maintaining the higher ratios of CTAB to n-hexanol. By increasing the concentration of hydrazine hydrate there was a decrease in size of NPs. The average diameter of Ni NPs of 4.6 nm shows superparamagnetic behaviour because of tiny size. The saturation magnetization (26.2 emu/g), remanent magnetization (0.67 emu/g) and the coercivity (7.5 Oe) were considerably smaller than those of bulk nickel (30). Similarly, Chen *et. al.,* synthesized Ni NPs of 12 nm ave. diameter with Face Centered Cubic structure using surfactant Cetyltrimethyl ammonium bromide, co-surfactant tetra dodecylammonium bromide and reducing agent hydrazine hydrate in appropriate amount of NaOH. The release of nitrogen gas during the reaction directly creates an inert atmosphere which prevents the formation of nickel oxide NPs and the size of superparamagnetic Ni NPs decreases with increase in the levels hydrazine hydrate because of whole amount of precursor gets reduced before nucleation (31). Xian *et. al.,* used water-in-oil emulsion for the synthesis of Ni NPs with various sizes and shapes using sodium borohydride as reducing agent and sodium dodecylsulfonate as stabilizing agent. The size of Ni NPs depends up on the emulsion constitution, concentration of water and surfactant, aging time, as the water-to-surfactant molar ratio increase the size of NPs also increase. When water-to-surfactant molar ratio is 9.5 the size of NPs is about 20 nm. The size of Ni NPs increases with aging time of emulsion and nickel ion concentration with less uniformity in particles distribution (32). Zhang *et. al.,* synthesized needle shaped fcc Ni NPs using hydrazine hydrate with a diameter of 6-8 nm and a length of 100 nm in the cationic microemulsion of water/CTAB, and n-butanol/n-octane (33).

Hydrothermal Method

Abdel-Aal *et. al.,* used hydrothermal method for the synthesis of Ni NPs in aqueous solution at 100°C and studied the morphology and size by changing the levels of surfactant CTAB, $NiCl_2$ and reaction time in the presence of NaOH and reducing agent hydrazine hydrate. The author declared that as the concentration of surfactant increases the particles size decreases by forming micelles and by changing the surfactant concentration there is a change in the morphology (34). Wang *et. al.,* reported the synthesis of Ni NPs by hydrothermal method by maintaining the inequality of white phosphorous in alkaline medium. The reductive agents are produced from the white phosphorous when it is in basic medium and TEM images reveals the average size of Ni NPs of about 26 nm (35).

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CONCLUSION

Nickel NPs have been synthesized by different techniques. The main drawback of these synthetic techniques is the oxidation of Ni NPs during synthesis. Due to this all the techniques have used organic solvents, toxic reducing agents like sodium borohydride, hydrazine hydrate and surfactants in their protocols. Very few authors have synthesized the NPs without using any toxic reducing agent in aqueous medium. More research is needed to develop synthesis method for the preparation of Ni NPs in industrial scale procedures without using toxic reducing agents. In this context synthetic techniques should be developed using green chemistry protocol with the help of non-toxic natural reducing and stabilizing agents such as plant materials, carbohydrates, aminioacids, proteins and microbes.

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An overview of Smart Materials in Nanoscience and Nanotechnology

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Abstract

Design of new materials with a multi-functional capability has become a key research focus in all materials science and engineering discipline in the recent past. A “smart material” is one having a structure at the nano-structural level that responds in a particular and controlled way to influences upon it. These range from magnetically-changed materials, to “memory” molecules that return to their original form, to materials that generate an electric charge when pressed, twisted, or warped. In some extent, a structure made by this material or more than one type of this material incorporated with an appropriated sensor system has been well defined as a “smart structure”, that can be used for the implementation of a damage and performance detection strategy for aerospace, civil and mechanical engineering and other applications. Since the last decade, an increasing interest in the development of miniaturized structures and systems, particularly on micro and nanoelectromechanical systems (MEMs and NEMs), and integrated biosensor systems has evolved a new page in the area of smart materials and nanotechnology.

Key Words : Functional Materials, MEMS, NEMS, Titanates, Shape Memory Alloys.

Pages: 6 **References: 14**

INTRODUCTION

Smart materials are demarcated as materials with properties engineered to change in a precise manner under the impact of external inducements in response to their environment[1 , 2] These external influences include thermal, mechanical, optical, magnetic fields, electric charge, force, moisture, pH. Recent examples of smart materials include self-healing polymers that release healing agents upon structural damage,[3,4] electronic paper displays, whose ink appears or disappears depending on electrical charge,[5] and meta-materials that serve as an “invisibility cloak” to make objects invisible at a particular wavelength.[6,7] smart materials may have a wide range of potential applications in medicine, and many of them, including thermoresponsive hydrogels,[8] switchable surfaces,[9] and photoresponsive materials,[10] have already been explored in this capacity. Smart materials are mainly classified into the following types,

a. Piezoelectric

b. Shape Memory Alloy

c. Optical fibre

d. Magnetostrictive

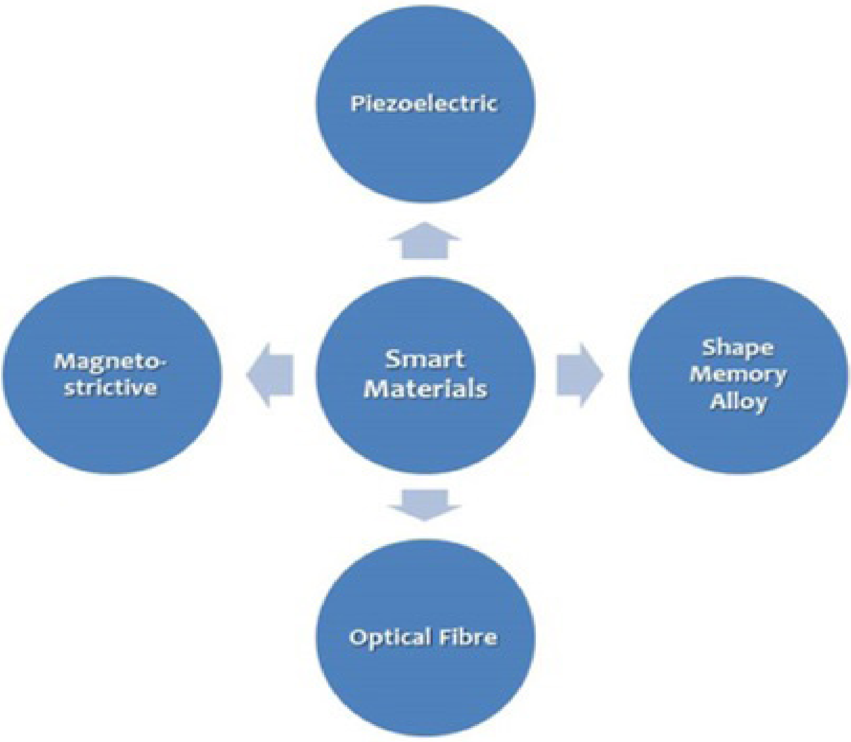


Fig. 1 Classification of Smart Materials

Piezoelectric

Piezoelectrics materials are used for both sensing and actuating devices which exhibit an electrical polarization with an applied mechanical stress (direct effect), or a dimensional change with an applied electric field (converse effect). When subjected to an electric charge or a variation in voltage, piezoelectric material will undergo some mechanical change, and vice versa. These events are called the direct and converse effects. Lead zirconate titanate ($PbZr_{1-x}TixO_3$) is the chief piezoelectric material as it may be doped to produce an n-type or p-type material with a range of dielectric constants to meet the requirements of numerous applications. Lead metaniobate ($PbNb_2O_6$), Barium titanate ($BaTiO_3$) and lead titanate ($PbTiO_3$) are other types of piezoelectric materials.

Shape memory alloys

Shape memory alloys are subjected to a mechanical load below a certain temperature these special materials will undergo phase transformations which will produce shape changes i.e., plastically deformed beyond their elastic limit but then are capable of retrieval their original shape if they are then heated above a certain temperature. Nickel-titanium is the best common Shape memory alloy with best shape memory properties having relatively low transformation temperatures, cannot match the outstanding shape memory capabilities of Ni-Ti. Cu-Zn-Al and Cu-Al-Ni are the common ternary Cu-based systems which can achieve commonly a shape memory strain of 4 to 5% (compared to about 8% for Ni-Ti) and have a broader range of transformation temperatures[11] Iron-based alloys like Fe-Mn, Fe-Mn-Si, Fe-Pt, Fe-Ni, Fe-Ni-Co and Fe-Pd exhibit shape memory but these are not capable of regaining their shape to the same extent as nickel-titanium and copper-based alloys.

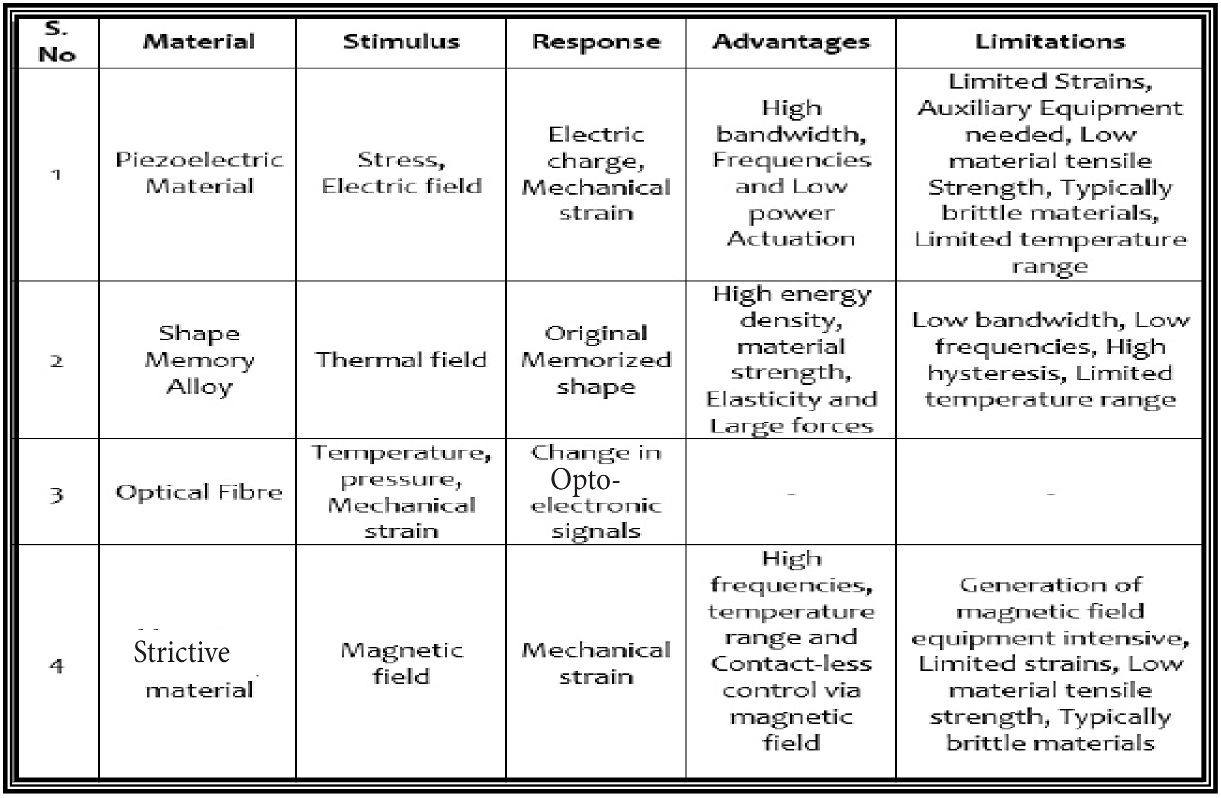
Magnetostrictive

When an external magnetic field is applied, magnetostrictive material will undergo an induced mechanical strain i.e., change in shape which is used in actuators contrary to this effect is called piezomagnetism which is used in sensors, where a magnetic field is produced/altered upon application of a mechanical strain. Ferromagnetic materials like Fe, Ni, Co etc. can exhibit magnetostriction to some extent and rare earth elements have exhibited considerably higher magnetostriction which limits to lower than room temperature. Nickel-based alloys and particulate composites are common magnetostrictive materials which contains magnetostrictive particles.

Optical Fibres

Optical Fibres are excellent sensors which use intensity, phase, frequency or polarization of modulation to measure strain, temperature, electrical/magnetic fields, pressure and other measurable quantities. The reaction for the incitement, advantages and disadvantages of various smart materials are tabulated in table1..

Table 1: Different Smart materials



S. No	Material	Stimulus	Response	Advantages	Limitations
1	Piezoelectric Material	Stress, Electric field	Electric charge, Mechanical strain	High bandwidth, Frequencies and Low power Actuation	Limited Strains, Auxiliary Equipment needed, Low material tensile Strength, Typically brittle materials, Limited temperature range
2	Shape Memory Alloy	Thermal field	Original Memorized shape	High energy density, material strength, Elasticity and Large forces	Low bandwidth, Low frequencies, High hysteresis, Limited temperature range
3	Optical Fibre	Temperature, pressure, Mechanical strain	Change in Opto-electronic signals	-	-
4	Strictive material	Magnetic field	Mechanical strain	High frequencies, temperature range and Contact-less control via magnetic field	Generation of magnetic field equipment intensive, Limited strains, Low material tensile strength, Typically brittle materials

Nanoscience and Nanotechnology

Today Nanoscience and Nanotechnology offer an incredible potential for the conceptual design and the practical realization of radically new smart materials that can help solve some of the global challenges. Nanotechnology is rapidly entering the world of smart materials and taking them to the next level. These new materials may incorporate nanosensors, nanocomputers and nanomachines into their structure. This will enable them to respond directly to their environment rather than make simple changes caused by the environment.

Applications of Smart Nanomaterial's

Smart materials are having prospective applications in medicine and many of them, including thermoresponsive hydrogels [12] switchable surfaces, [13] and photo-responsive materials. [14] Another prominent motivation of the quest for synthetic materials with dynamically controlled properties is their potential use as dynamic blueprints in time-resolved self-assembly.

In the future scientists may be able to produce nanoparticles that can be incorporated in paints to efficiently capture solar light and convert it into electric energy at a low cost; or nanomaterials that can allow the design of new batteries with high power content and light weight. Nanoelectronic devices like nanocomputers that can be incorporated in textiles and clothing and provide new functions like a change in hardness as a consequence of an impact. Probably, the field where smart nanomaterials are going to have the largest impact is in healthcare and medicine. Implants and prostheses made from materials that can modify their surfaces and biofunctionality to increase biocompatibility; or specific functionalized nanoparticles that are able to deliver drugs and antibiotics in specific areas of a living organism; or synthetic "cells" that can produce protein drugs when triggered with light.

Despite this encouraging progress, the implementation of switchable properties will continue to be one of the central obstacles in nanomaterial's science in the decades to come. Ultimately, imparting dynamic properties to nanomaterials will result in systems where the materials themselves will be the actual active device.

a. Energy generation and conservation with highly efficient batteries and energy generating materials.

b. Security and Terrorism Defence with smart materials that can detect toxins and either render them neutral, warn people nearby or protect them from it.

c. Healthcare, with smart materials that respond to injuries by delivering drugs and antibiotics or by hardening to produce a cast on a broken limb.

d. Implants and prostheses made from materials that modify surfaces and bio-functionality to increase biocompatibility.

e. Smart textiles that can change colour, such as camouflage materials that change colour and pattern depending upon the appearance of the surrounding environment. These materials may even project an image of what is behind the person in order to render them invisible.

CONCLUSION

Smart materials have already been used and are now an intrinsic part of our society. Nanoscience and nanotechnology is essential for the development for smart materials, acting as a tool which can change the properties of structures and involved in development of smart materials. Nanoscience and nanotechnology today offer an incredible potential for the intangible design and the practical realization of fundamentally new smart materials that can help solve some of the potential global societal challenges. Nanotechnology and smart materials are crucial for future technology developments and it will directly and indirectly impact our everyday life sooner or later. Though some people argue that smart materials are from nature and they can survive themselves and nanoscience and nanotechnology is not necessary for development for smart materials. Nanotechnology and Smart Materials provides together provides plethora of advantages where engineers and scientists working on nanoscience and nanotechnology and smart materials all around the world freely get together and discuss.

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Review on Bio-based Polymer Beads and Their Applications

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Abstract

The modification of bio-polymeric materials like cellulose, chitosan, agar and agarose are more useful for increasing applications in biochemistry and other areas like chemical engineering and biotechnology with improved properties. Polysaccharides beads show more biocompatibility and sustainability after chemical modification. Cellulose bio-polymer hydrogel beads are extensively used for supporting enzymes entrapment and other potential advantages like bio-fuel cells, bio-sensors and tissue engineering due to their nature of bio-degradability and bio-sensitivity.

Key Words : Bio-Polymeric Materials, Polysaccharides Beads, Cellulose Bio- Polymer Hydrogel Beads.

Pages:14 **References:136**

INTRODUCTION

Chemical design of biobased materials needs modification and functionalization to tune their properties such as hydrophobicity, hydrophilicity and inertness for better solubility and processibility. Although polysaccharides have excellent mechanical and chemical properties as well as abundance, biocompatible, and sustainable in nature (1-4), chemical modification makes them from hydrophilic to hydrophobic and from noncharged to anionic or cationic (5-7). Normally cellulose beads (~ 10 µm to 2-3 mm diameter) are used in versatile applications such as drug carriers, adsorbent support, metal ion exchange and water treatment, solid-supported synthesis and protein immobilization related applications. Several methods and techniques have been developed for the preparation of advanced cellulose materials and cellulose bead in both batch and pilot scales by varying solvents, shaping agents, chemical functionalization or blending with various inorganic and organic compounds using novel cellulose solvents such as ionic liquids and aqueous systems in micrometer to millimeter scale.

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CELLULOSE BEADS

In literature cellulose beads have frequently been named: microspheres, pellets, cellulose gels, pearl cellulose, or beaded cellulose. The present discussion will concentrate only beads prepared from cellulose solution after dissolution, shaping and regeneration of cellulose. Beads or spheres prepared from cellulose suspension possess different type of microscopic morphology i.e. pore structure. In addition, functional cellulose beads may use other polysaccharides or its derivatives after incorporation of inorganic/organic compounds by heterogeneous chemical modifications of cellulose. Cellulose possesses three hydroxyl groups per repeating unit that are accessible for chemical modification. Chemical modifications such as etherification, esterification, oxidation and polymer grafting; blending with other polysaccharides are used for dissolution and beads formation.

If direct binding of a specific functional group to cellulose is not always possible due to inactivity of desired molecule with hydroxyl groups, some activated molecules (i.e. thiolysed alkenes, oxirane attachment to cellulose, amines and carbonyl attachment to cellulose, cellulose hydroxyl to tosyl or chlorides, attachment of cross-linkable groups, cationic/anionic groups, affinity/hydrophobic groups, etc.) formed by bridging more active molecule to cellulose are prepared and converted to beads in situ in which the main matrix remains cellulose as the major component. Also, beads (like calcium alginate gels) prepared exclusively from cellulose derivatives/blends followed by stabilization using ionic liquids are controlled by ionic interactions.

Preparation of cellulose beads consist of three steps i.e. i) dissolution of cellulose or its derivatives, 2) shaping into spherical particles in solution and 3) sol-gel transition and solidification of the solution particles to beads in a coagulation bath of a nonsolvent. Sometimes, several post- and pretreatments are done to fine-tune some properties of the beads. After dissolution shaping step is carried out by different techniques such as dropping (by mechanical deformation), jet cutting, spinning drop atomization, spinning disc atomization and dispersion (by applying high centrifugal forces). Dropping techniques result beads diameter of ~ 0.5-3 mm. When the droplets hit the surface of the coagulation bath, the mechanical strain developed surrounding droplets determines the length to width factor of beads and the stability of the droplets depends upon the applied force. If the applied force is higher, flattening of the beads may occur and results a disk-like shape. Optimization of falling height, solution viscosity, and ejection speed controls the size and shape of cellulose beads in a dropping technique (8, 9). In dispersion technique dispersion of a solution of cellulose or a cellulose derivative in an immiscible solvent of opposite polarity under high rotational speed is made and the emulsion formed is stabilized with the aid of surfactants (10). Cellulose beads (~ 30-250 μm) prepared by dispersion are roughly 10-times smaller compared to those prepared by dropping techniques.

By spinning disc atomization droplet is formed when a thin film of the polymer solution is constantly spread onto a ro-

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tating disc and ejected from the edge as a result of centrifugal forces (11, 12). It is established that cellulose possesses an exceptionally strong inter- and intramolecular hydrogen bonding network which makes cellulose insoluble in water and common organic solvents (1, 13). By coagulation in an excess of protic nonsolvent regeneration of the polysaccharide is carried out by disturbing physical interactions, but non-derivatizing solvents dissolves cellulose by physical interactions instead of the chemical conversion of its hydroxyl groups (14).

The derivatizing solvents temporarily convert cellulose into metastable intermediate derivatives under the dissolution conditions. Metastable cellulose derivatives can be regenerated into fibers or beads by cleavage of the intermediate derivatives induced by the addition of water or a change in pH or temperature. Cellulose is converted into cellulose xanthate (CXA) by a sequence of alkalization, aging, and CS_2 treatment (viscose process) (15-17) which is soluble in aqueous NaOH/urea/ionic liquids. Regeneration of polysaccharides is done by acid treatment or by increasing the temperature (90 °C for several minutes). Now-a-days cellulose carbonate (CC) which is soluble in NaOH is shaped into fibers by acid hydrolysis and into beads by dropping or dispersion techniques (18, 19).

But stable cellulose derivatives (e.g. cellulose acetate) are soluble in common organic solvents (such as chlorinated hydrocarbons or ethyl acetate) which are regenerated by coagulation or evaporation of the solvent in the presence of a non-solvent (20, 21). In non-derivatizing solvents, the auxiliary substituent needs forced hydrolysis step during this process and hence an additional process step is carried out to prepare cellulose beads from the shaped derivatives. Unlike xanthate and carbamate groups, the acetyl moiety is not cleaved during the regeneration process. Hence cellulose acetate (CA) needs an additional step to convert cellulose derivative in which precipitation is carried out by displacing the organic solvent with a nonsolvent such as water. Analogous to CA, trimethylsilyl cellulose (TMSC) has been utilized for the preparation of cellulose beads by the dispersion technique (22). Moreover, introduction and removal of acetyl or silyl moieties by saponification, or cleaving the acid labile silyl ether by acid treatment are needed for cellulose derivatives as the starting materials. The direct dissolution of cellulose, without chemical modification of the polysaccharide, and subsequent coagulation in a nonsolvent is the most convenient method for producing cellulose beads.

Classical non-derivatising solvents such cuprammonium hydroxide (cuoxam) and aqueous metal salt solutions of copper, cadmium, nickel, iron, and cobalt containing coligands such as ammonia, ethylene diamine, or tartaric acid, can dissolve cellulose via complexation of its hydroxyl groups (23, 24). These are not used currently due the presence of heavy metals. Similarly cellulose dissolves in N,N-dimethylacetamide (DMA) containing LiCl and is used for the chemical derivatization of the polysaccharide under homogeneous conditions (25, 26), but due to the high costs of the solvent and the limited recyclability DMA/LiCl is not popular for the preparation of cellulose beads. N-methylmorpholine N-oxide monohydrate (NMMO), an alternate to viscose process, is the most frequently applied non-derivatizing cellulose solvent for the preparation of cellulose fibers (27). Cellulose/NMMO solutions crystallize at temperatures around 20-40 °C by dropping or dispersion techniques (28) and NMMO residues are removed from the preshaped particles by water washing (29-34). It has some disadvantages such as thermally unstable upon mixed with activated carbon, magnetic particles and other polysaccharide derivatives (35, 36).

Aqueous NaOH solutions with gelation preventive additives such as urea, thiourea, or ZnO, have gained much interest in this context (37-40). Cellulose dissolves in these aqueous solutions at around 10 °C and can be regenerated by coagulation in diluted acids. But these aqueous cellulose solutions must have low solution viscosities to get low polymer concentration and degree of polymerization (DP) which is essential for shaping during dropping technique. Some efficient pretreatment techniques have been developed to improve the solubility of cellulose in aqueous NaOH solution (41-43) and successfully is used to prepare beads by dropping, spinning drop atomization and dispersion techniques with or without additives such as urea, thiourea or polysaccharide derivatives (10, 44-46).

Ionic liquids (ILs), promising type of novel cellulose solvents, are molten organic salts with melting points below 100 °C and can dissolve cellulose (48-50). Spinning of fibers, biorefinery and conversion of lignocellulosic biomass, and chemical modification of polysaccharides are done using ILs (51-54). Dispersion and dropping techniques have used imidazolium-based ILs for the preparation of cellulose beads (55-57). Other polysaccharides such as chitosan, agarose and various artificial polymers also dissolve in ILs and can be used to prepare cellulose composite beads (58-61). But high viscosity of cellulose/IL solutions (62, 63) requires sophisticated technical devices such as an underwater pelletizer for their processing (55), efficient recycling strategies (54, 64) and complete removal of IL residues from regenerated cellulose for successful adaptation (6).

Several process parameters need to be controlled during beads formation. Size of beads, density, surface area, and pore size structure are controlled by coagulation process. It is possible to changeover dissolved polysaccharide to solid particles followed by bead formation and change in morphology by simply switching process parameters (8). In general, cellulose concentration controls porosity of the beads, while temperature and composition of coagulation medium monitors other physical parameters such as morphology, internal surface area, and pore size distribution. It is possible to tune chemical and adsorption properties of cellulose beads by chemical modification. Normally inorganic additives control the physical properties of cellulose beads. The density of cellulose beads is increased from $1g/cm^3$ to $2.5g/cm^3$ by mixing with dense particles of TiO_2, tungsten carbide, nickel, or stainless steel powder (34, 57, 65-68). Also, magnetic cellulose beads are used to remove arsenic and other contaminants from environmental samples after proper chemical modifications with tailored properties (69, 70). Sometimes beads with macroscopic pores are prepared after removal of inorganic additives such as Na_2SO_4 or $CaCO_3$ by washing with aqueous solutions (71-74).

Also, polysaccharide starch can be removed from cellulose beads by amylase treatment which generates a porous material (68) and enzymatic hydrolysis of pure cellulose beads with cellulose increase the pore diameter (75). In addition, blowing agents such as $NaHCO_3$ or azodicarbonamide can decompose under the liberation of inert gases during coagulation process (76) resulting macroscopic pores. Total porosity is only an indication of the empty space in beads, but it does not necessarily correspond to the amount of accessible pores or their size distribution. Mercury intrusion can measure pores from 2 nm up to several hundreds of µm and nitrogen sorption from 0.3 to 300 nm. Solute exclusion using dextran or polyethyleneglycol (PEG) macromolecules of defined molecular weight is used for direct quantification of the pores of different sizes within cellulose beads (8, 77). About 1-56 nm for dextran and 0.7-5.7 nm for PEGs sized solute can be excluded which provides a discontinuous distribution. However, direct information on size exclusion properties is valuable for applications in size exclusion chromatography.

Due to unequal growth along the edge a non-uniform morphology results on the surface. Lyophilization cannot be applied during characterization of beads morphology because volume expansion of water upon freezing and the growth of icecrystals cause the collapse of the micro- and mesopore in cellulose beads (18). Hence critical point (CP) drying is practiced for the characterization of beads morphology since morphology is preserved due to prompt removal of solvents (8, 18) and water is stepwise exchanged by ethanol, acetone, and finally liquid CO_2, which is removed under supercritical conditions. High porosity of cellulose beads make them versatile agent in different applications. As per porosity cellulose beads are classified as micro- (<2 µm), meso- (2-50 µm) or macropores beads (>50 µm) (78).

Cellulose beads are not rigid but are elastic and compressible to a certain extent. Based on tuning of size, physical properties and chemical modifications cellulose beads i.e. functional cellulose beads are versatile materials and are used in different applications such as chromatography, metal ion exchange and water treatment, protein immobilization, solid-phase synthesis supports, and drug loading and release i.e. different drug delivery applications.

Further developments in the field of functional cellulose beads are needed for its different applications with novel and improved properties. Functional hybrid materials of blending cellulose with highly engineered polysaccharide derivatives promise great potential in future applications which needs thorough and in-depth research.

Agar based beads

In the mid-seventeenth century agar was discovered in Japan and the main source

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for agar was thalloid alga *Gelidium*. Compared to other gelling agents gelation of agar occurs at temperature below its gel's melting point (~85-95°C) (79). The component of natural polysaccharide, agaropectin is nothing but a non-gelling ionic (charged) polysaccharide which is present within the agar extract (79). Normally agar sol sets to a gel at about 30–40°C and maintains it shape with 0.1% agar. Agar does not degrade by the most microbial organisms and it is used as growth supporting materials in all microbiological studies.

Beads are prepared by the traditional techniques such as dropping or dispersion of molten sol into ice-cold fluid or pouring into the preheating vegetable oil followed by cooling to 5°C with stirring (80). Degree of agitation determines the size of the resultant gel beads (81). Banerjee *et. al.* described a dropping method for agar beads in which agar solution was poured into an ice-cold mixture of chloroform and toluene (1:3 v/v) at 45–50°C followed by cleaning with phosphate buffer and mechanical strength was developed by air-drying (82). The shape of all beads is retained by coating a polymer which is water-soluble, preferably aquaternized cationic polymers such as steardimonium, polyquaternium and hydroxyethylcellulose. Also, these restraining polymers can bind with various active agents such as lactic acid, ascorbic acid (81).

Now-a-days several process industries such as cosmetics, personal care, and neutraceutical, affinity chromatography, and immobilization processes are consuming agar beads.

Agarose based beads

Agarose, a natural polysaccharide obtained from red seaweeds, contains alternating residues 1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-α-L-galactopyranose (83). Agarose is a type of polysaccharide which forms gels and don't contain sulfate. It is neutral (non-ionic) polysaccharide and is different from non-gelling ionic (charged) polysaccharide, agar containing agaropectin (79). The percentage of agarose in agar-bearing seaweed is 50–90% (84). Agarose's melting point is ~90 °C and its molecular weight 105 Da, but its gel is formed by lowering the temperature of the heated agarose to lower than 40 °C. Earlier suspension gelation [85] and spraying gelation (86, 87) were used to prepare spherical agarose beads using different surfactants, but it was difficult to control distribution of beads. Due to this problem application of non-uniform beads was limited to their uses in chromatography because uncontrollable flow rate and backpressure caused non-reliable results.

Microporous membrane emulsification technique is also used to prepare uniform-sized agarose beads from agarose aqueous solution containing 0.9% sodium chloride (88). A uniform Water/Oil emulsion prepared from liquid paraffin and petroleum ether containing 4 wt% of hexaglycerin penta ester (PO-500) is used to form gel beads after cooling under gentle agitation. This can prepare uniform agarose beads with diameter from 15 to 60 μm.

Agarose is costlier than agar and hence it is used as a base material for electrophoresis in biotechnological applications and as a filter for gel filtration (89). Agarose can be used not only for manufacturing beads for cell encapsulation but also as a bead coating (90).

Alginate based beads

Alginate, a commonly used material to encapsulate probiotics, is a naturally occurring biocompatible and biodegradable linear anionic polysaccharide. Alginic acid is a linear copolymer composed of D-mannuronic acid (M) and L-guluronic acid (G) (91, 92) which is known as algin or alginate. Being an anionic polysaccharide forms viscous gum with water and distributed widely in the cell walls of brown algae. Alginates are widely used in foods as a viscosity modifier, stabilizer, thickener, and emulsifier. Alginate forms gels with a number of divalent cations (93).

Crosslinking is used to modify properties of alginate. Crosslinking takes place via carboxyl groups by primary valences and via hydroxyl groups by secondary valences (79). For immobilization studies agarose gel strength is increased by using aluminum nitrate (trivalent cations) (94). Out of many procedures nozzle ring sprayer is used for the preparation of gels from gum solution in the presence of cross-linking solution (95). Production of beads with controllable sizes (~ 0.5–3.0 mm) is possible (96).

Lotfipour *et. al.* has prepared alginate beads by extrusion/emulsion technique within a range of 1.59 ± 0.04 to 1.67±0.09 mm (97). Its susceptibility to disintegration in the presence of excess monovalent ions, Ca^{2+} chelating agents, and harsh chemical environments causes difficulty in actual applications (98). Liu *et. al.* used emulsification coupled with internal gelation method for the preparation of spherical calcium alginate gel beads (99). The size of the beads was about 50 μm. In this process the size of the beads was mainly dependent on the diameter of the membrane pores and concentration of sodium alginate where low concentration leads to non-spherical beads and high concentrations lead to higher sized beads. By droplet method lower than 200 μm beads are not possible to prepare whereas emulsification method can prepare smaller sized beads with a wide variation.

Due to non-toxicity of calcium alginate is widely used in food and biotechnological applications. Also, other divalent cations, such as Cu^{2+}, Ba^{2+}, or Pb^{2+} have a greater affinity to alginate than Ca^{2+}, but their toxicity limits their fields of application. Recently alginate bead are prepared for adenovirus delivery in sustained manner (100) using electrospraying technique. Also, integrated alginate beads are used to immobilize hepatocytes for bioartificial liver use (101).

Interestingly alginate beads are used as a base for culturing common primary liver cancer cells to study hepatocellular carcinoma (HCC) which often forms metastases which causes enormous failure in chemotherapeutic treatment. It is found that in vitro invasion assay has showed that the invasion cells derived from ALG beads was 7.8-fold higher than adhesion cells (102). Also, reinforced silica-alginate beads are used for a 3D cell culture system using Chinese hamster ovary (CHO) cells (103).

Chitosan based beads

Commercial chitosan is prepared from the shells of shrimp and other sea crustaceans after deacetylation of the N-acyl group in chitin by chemical treatment. In addition, it has been demonstrated that β-chitin exhibits much higher reactivity in deacetylation than α-chitin (104). Reacetylation, up to 51%, of a highly deacetylated chitin using acetic anhydride gives a water soluble derivative, but partial deacetylation of chitin results acid-soluble product or even insoluble product (105).

Chitosan is biologically safe, non-toxic, biocompatible and biodegradable polysaccharide. They become soft and rubbery in the swollen state which resembles living tissues. Hydrogels exhibit good biocompatibility and they are highly responsive to temperature, pH, electrical pulses, etc. Chitosan being positively charged binds negatively charged surfaces and its charge density depends on pH and degree of deacetylation. It is good candidate for site-specific drug delivey. Chitosan-based hydrogels (beads) are used numerous drug delivery systems such as colon delivery (106), oral delivery (107, 108), ophthalmic delivery (109), nasal delivery (110), buccal delivery (111), vaginal delivery (112), because these beads are the cross-linked three-dimensional network polymers which swell, but do not dissolve in water. Advances in the field of chitosan gelation promote biomedical applications that use microgel or nanogel particles for drug delivery (113). These chitosan-based beads are essentially employed for the slow release of the drugs a particular target site to improve the therapeutic activity. Also, chitosan–glycerol–water gel or gel-like membrane is useful as a carrier for medications to be applied to wounds (114).

Acidic polysaccharides were considered as the troublesome dissolved substances. Prominent among these acidic polysaccharides were pectins, or polygalacturonic acids (PGA) (115). Chitoson has high affinity to proteins and possess reactive surface functional groups for direct reactions with enzymes and for chemical modifications, hydrophilicity and mechanical stability (116). Using these properties immobilization of different enzymes has been carried out on chitosan beads (117, 118) in abating environmental pollution. In addition, these beads are able to absorb transition metals, anions and organic species via amino and hydroxyl groups (119-127). There has been increasing interest in using alginate-chitosan microcapsules as the drug-delivery systems of proteins and polypeptides (128-132).

Carrageenan based beads

Gum is a family of agar, furcellaran, and three types of carrageenan (κ, ι, and λ) and mainly prepared from red seeweed. Due to difference in chemical structure carrageenans are soluble in water above 75 °C. Although sodium salts of κ- and ι-carrageenan are soluble in cold water, their calcium and potassium salts exhibit varying degrees of swelling and do not dissolve completely, whereas λ-carrageenan is fully soluble in cold water (79). By crystallization or precipitation carrageenam gels (beads) are prepared from their solution after proper heat treatment (~ 80 °C). In the presence of positively charged alkaline metals beads are formed on cooling. Extrusion through an orifice or hollow needle (dripping method) and dispersion in liquid or air it is possible to control shapes such as cubes, beads, or membranes during manufacturing. The strength of the beads can be tuned with chlorohydrins, diepoxides, glutaraldehyde, tannin, or polyamines (133) or by adding Al^{3+} cations (134).

Crosslinked carrageenan beads can be used as a controlled-release delivery system. Epichlorohydrin is a well-known crosslinker for polysaccharides and low concentrations of epichlorohydrin led to unstable and weak beads with uneven, cracked surfaces. Hence, the concentration and type of cross-linker play a vital role in controlling size, morphology and surface topography of beads (135). This type of beads has great potential for their application as delivery systems in food or pharmaceutical products. It is observed that carrageenan beads are superior to agar and inferior to calcium alginate (136).

CONCLUSION

Bio-polymer based beads are versatile materials for many advantages. In now-a-days increasing interest on biobased materials is emerging as rapid increase in research in polysaccharide family. New methods and advanced procedures for efficient dissolution of bio-components and control of process parameters for shaping and size tuning of beads are urgently needed for selective application in reliable and reproducible manner.

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Green synthesis of Platinum Nanoparticles – a review

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Abstract

Platinum (Pt) is one of the important noble metals and its nano form is used in many chemical, physical, electrical and biological applications. Different chemical and physical methods have been used in the synthesis of Pt nanoparticles (Pt NPs) which are reported to be time consuming, expensive and use of harsh chemicals in synthetic procedures. Since Pt NPs have been used in wide range of applications including human contacting applications, there is an increasing demand for the production of NPs in large scale. In order to come out from above mentioned problem and also to produce green and safer materials in nano science researchers opted green chemistry which involves the use of natural products for the synthesis of metal NPs. In recent years production of metal nanoparticles by green routs has gained lot of attention because of its advantages over other conventional techniques. Synthesis of different metal nanoparticles and metal nano composites using various bio-reducing agents such as plant extracts, bacteria, fungi and yeast has been reported. This review describes the advancements in the green synthesis of Pt NPs using different biomolecules and synthetic biocompatible agents.

Key Words : Platinum, Biological Synthesis, Microorganisms, Plant Extracts.

Pages:17 References: 74

INTRODUCTION

Nanotechnology has become one of the most important areas to the researches belonging to various disciplines such as chemistry, physics, biotechnology, and electronics etc. due to its enormous potential towards diverse sectors such as agriculture, healthcare, environment and energy (1). From past decade nanotechnology is gaining great momentum due to its ability to produce materials in nanoscale and their applications in different areas, hence there has been a notable research attention in the synthesis of various metal NPs including both organic and inorganic in nature. Organic NPs include carbon based materials (graphene oxide, graphene, CNT, fullerenes) and inorganic NPs include nano forms of noble metals (gold, silver, palladium and platinum), magnetic materials (iron, nickel and cobalt) and semiconductors (zinc oxide, zirconium oxide and titanium dioxide). Nanoparticles are of great interest due to their very small size and high surface to volume ratio which differs them in physical, electrical, thermal, electronic, mechanical, optical, magnetic, chemical and biological properties as opposed to bulk materials (2). Among the above mentioned nanomaterials noble metal NPs have lot of significance due to their unique properties (chemical, optical, electrical, magnetic and mechanical) which leads to numerous applications in different technological and biological areas such as catalysis (3), cell tracking (4), photo catalysis (5), DNA detection (6), bio-labeling (7), optoelectronics (8) and imaging (9). There has been mounting curiosity for the design of NPs with an intricate shape and controlled size under ambient conditions in aqueous solutions. There are various routes of synthesis of metal NPs which is generally classified into 2 forms i.e. top-down approach and bottom-up approach. In top-down approach the larger molecules are reduced to nanosize whereas in bottom-up approach involves reduction from the atomic/molecular scale to the nanoscale.

Based on conversion procedure, different methods are categorized into above mentioned forms (Figure - 1). Various physical and chemical methods are employed for the preparation of noble metal NPs which involves reduction of metal ions in a solution by chemical reducing agents such as $NaBH_4$ (10), potassium bitartrate (11) and ethylene glycols (12). Both flexible and rigid templates such as micelles (13) and mesoporous silica (14) have been successfully used for preparing the nanostructures. A number of physical methods including UV-irradiated photo-reduction (15), sonochemical (16), microwave assisted (17), arc discharge (18) and polyol processes (19) have also been reported. Although physical techniques produce well defined nanomaterials (identical size, shape, composition and dispersion) than chemical methods, these methods are expensive and time consuming. Formation of metal NPs by chemical methods requires short period of time for large quantity of NPs, but this method is concerned with stability issues in aqueous solutions and requires additional stabilizing agents. Without stabilizing agent particle aggregation is noticed due to van-der Waal's forces of attraction (20). Hence a few number of synthetic stabilizing/capping agents such as polyvinylpyrrolidone (21) and sodium polyacrylate (22) have been used, but these stabilizing agents lead to particle deformation (23), reduced activity (24), growth inhibition (25) of the NPs and also in many cases the reducing agents used for reduction and capping agents for protection lead to production of toxic and non-ecofriendly byproducts.

Environmental protection being key issue for our society in present generation, also in order to minimize/eliminate waste during the design and process of reactions in the emerging areas of nano science, researchers have adopted green synthesis (26). It is well-known that green synthesis is based on 12 green chemistry principles which explore chemistry techniques and methodologies that reduce or purge the use of reagents, etc. which are harmful to human health or the environment and also production of environmentally friendly materials by using green reducing agents (solvent, reducing agent, stabilizing agent), simultaneously designing of the mild reaction pathways (low temperature, pressure, pH) (27-29). Noble metal NPs have been widely used in biomedical applications which plays vital role in drug delivery, imaging, sensing and diagnostics, hence above concept of green chemistry is becoming one of the main goals of designing new process and reaction in the synthesis of various metal NPs. Biological material such as bacteria, yeast, fungi and plants are regarded as persuasive ecofriendly green nanofactories (30, 31), because of their multifunctional nature (acts as both reducing and capping agents) and have been used extensively for the fabrication of NPs. Many researchers have demonstrated the use of various phototrophic eukaryotes for the synthesis of Au and Ag NPs, but only few reports are available on the biosynthesis of Pt NPs. This review provides a precis of existing works on the biosynthesis of Pt NPs using green chemicals, micro organisms, plants and presents some of the important results that can be used for the advanced studies.

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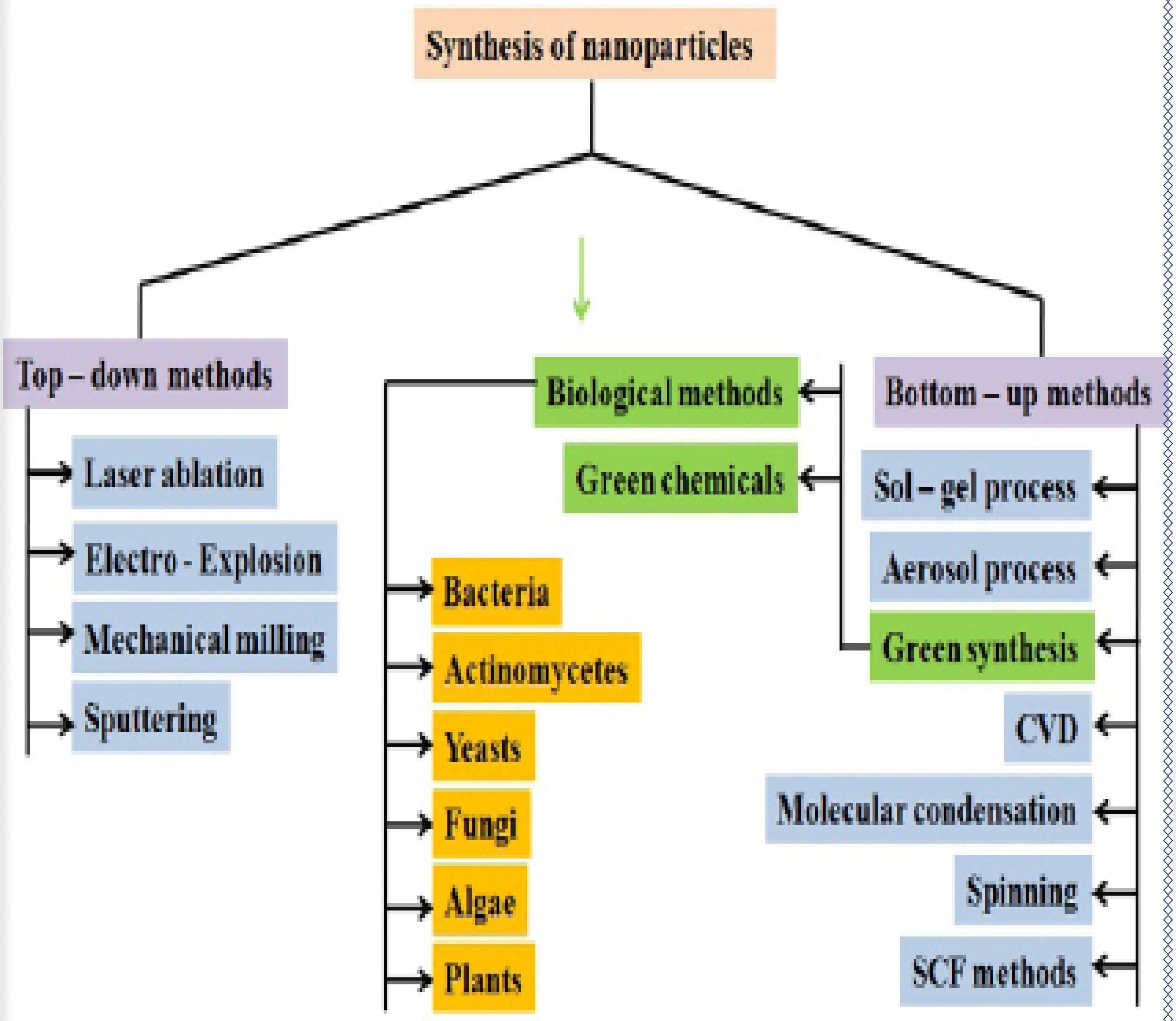

Figure 1: methods used for the synthesis of nanoparticles.

Importance of Pt NPs

Nanoparticles have a greater surface area per weight i.e. surface to volume ratio than bulk material and this property makes them to more reactive than other molecules; hence they are used or being evaluated for use in many fields. Noble metal NPs (Ag, Au, Pd and Pt) are widely used in many areas because of their potential applications. Among these metals, platinum has high melting point (1769°C), corrosion resistance and stability towards oxidation at high temperatures which plays a major role in many industrial applications and automotive catalysts (32, 33). Owing to both primary and scientific importance, Pt NPs has been the major focus of interest which plays a key role in many applications (Figure - 2) such as bioanalysis (34), catalysis (35), electro-optical devices (36), surface-enhanced Raman scattering (SERS) (37), magnetic devices (38), efficient catalysts in many organic reactions such as redox reactions (39), hydrogenation reactions such as hydrogenation of o-chloronitrobenzene to o-chloroaniline (40) and cinnamaldehyde to cinnamyl alcohol (41). Recently it has been reported that Pt NPs have shown similar activity to that of oxidizing NADH and reducing coenzyme Q (42). Pt NPs also have been used as catalyst in polymer electrolyte fuel cells and direct methanol fuel cells (43) and also in the preparation of organic dyes (44). Compared with other metal NPs, Pt NPs are especially appealing in catalysis, because gases such as hydrogen, oxygen and others will easily bind to platinum, for example Pt nanocrystals directly catalyze H_2O_2-mediated oxidation of 3, 3′, 5,5′- tetramethylbenzidine (TMB) with high catalytic activity (45). Uses of Pt NPs in automobile as catalysts to reduce nitrogen oxides to nitrogen gas, and to oxidize carbon monoxide and hydrocarbons to carbon dioxide and water has been reported. On the other hand Pt-containing compound, cisplatin (cis-diaminedichloroplatinum) has been used as antitumor agent (46) and nanocrystals of FePt@CoS_2 are found to be more potent in killing HeLa cells (47). Pt NPs along with other non-metals in the form of bimetallic, alloys or in core-shell forms have been used in biomedical applications.

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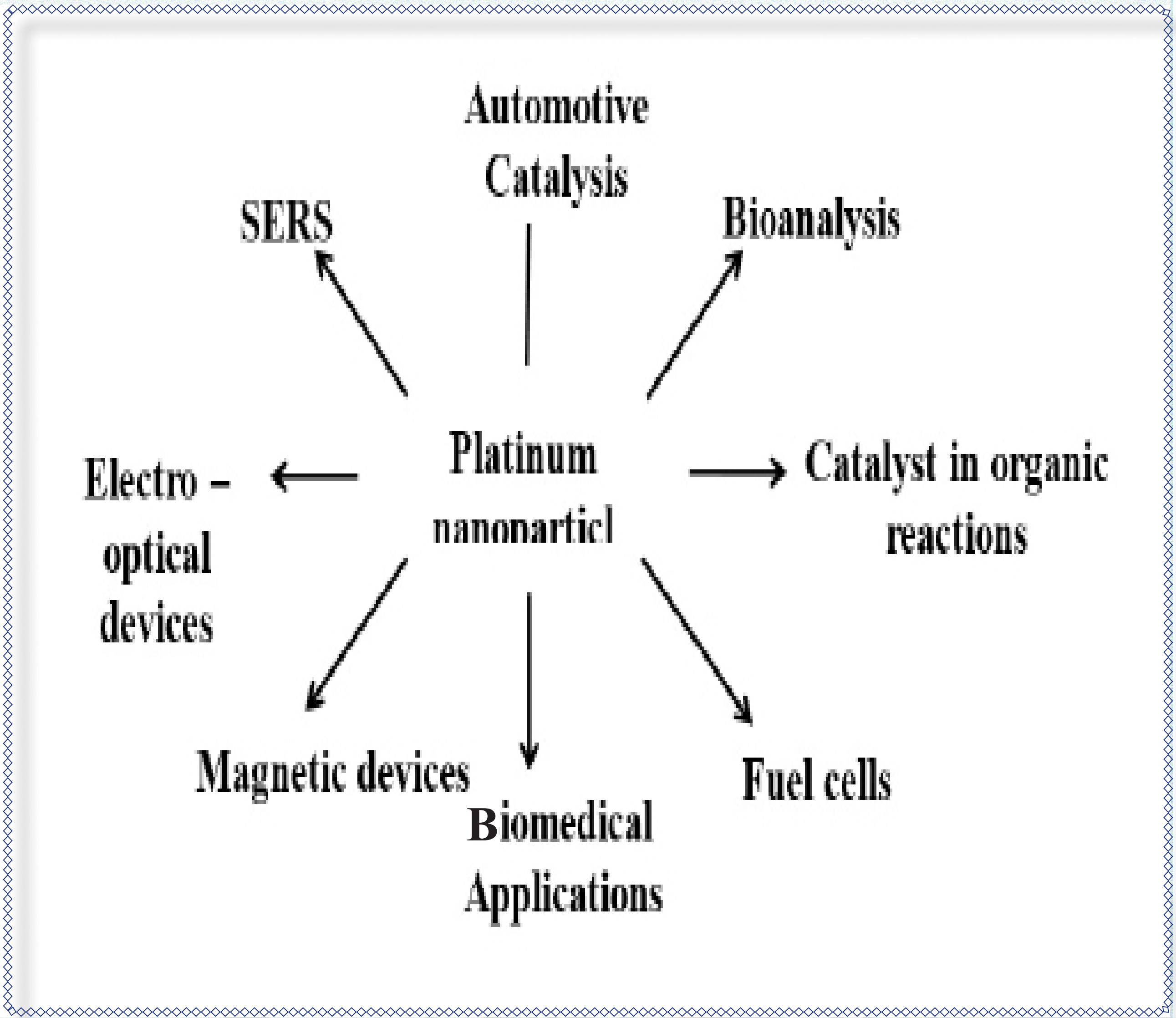
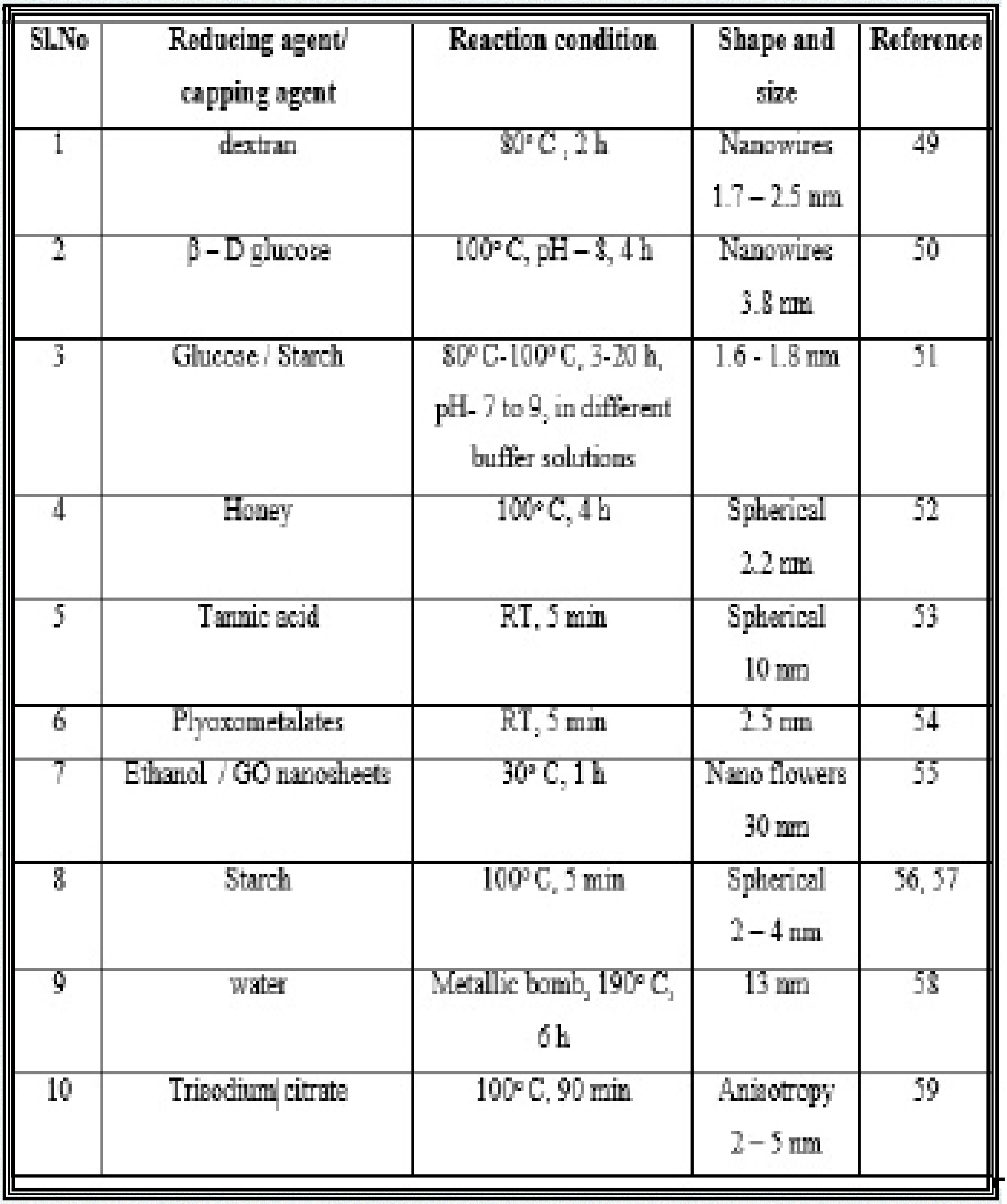


Figure 2: Applications of platinum nanoparticles.

Synthesis of Pt NPs using green chemicals

Various synthetic green reducing/capping agents have been employed for the synthesis of Pt NPs which are summarized in Table 1. Wen Yang *et. al*., (48) has reported synthesis of mono-dispersed Pt NPs using aminodextran as the reductive and protective agent after heating at 80°C for 2h. The authors also have reported that by changing the concentration of aminodextran the size of the NPs can be tuned and Pt nanowires like structures with the ratio 23:1 (dextrane : Platinum) at 80°C for 2h using dextrane as reducing and stabilizing agent were synthesized in the size range from 1.7 to 2.5 nm (49). Yongsoon Shin *et. al*., (50) used β-D- glucose for the synthesis of Pt NPs in sealed autoclaves under hydrothermal conditions at pH 8

Table 1: Synthesis of Pt NPs using green chemicals as reducing and stabilizing agents



Sl.No	Reducing agent/ capping agent	Reaction condition	Shape and size	Reference
1	dextran	80° C , 2 h	Nanowires 1.7 – 2.5 nm	49
2	β – D glucose	100° C, pH – 8, 4 h	Nanowires 3.8 nm	50
3	Glucose / Starch	80° C-100° C, 3-20 h, pH- 7 to 9, in different buffer solutions	1.6 - 1.8 nm	51
4	Honey	100° C, 4 h	Spherical 2.2 nm	52
5	Tannic acid	RT, 5 min	Spherical 10 nm	53
6	Plyoxometalates	RT, 5 min	2.5 nm	54
7	Ethanol / GO nanosheets	30° C, 1 h	Nano flowers 30 nm	55
8	Starch	100° C, 5 min	Spherical 2 – 4 nm	56, 57
9	water	Metallic bomb, 190° C, 6 h	13 nm	58
10	Trisodium citrate	100° C, 90 min	Anisotropy 2 – 5 nm	59

and 100°C. Formation of stable Pt NPs with average particle size of 3.8 nm at 4h, while the reaction time increased from 4 – 24 h larger size nano clusters of 200 nm was reported (49). As the reaction proceeds reduced Pt NPs undergoe self assembly to form loosely packed arrays and finally leading to the evolution of nanowires. Monodisperse Pt NPs using glucose as a reducing agent and starch as a stabilization agent in three different buffer solutions namely 2-(N-morpholino) ethanesulfonic acid (MES), ammonium acetate and phosphate with the pH ranging of 7-9 at 80-100°C for a duration of 3-20h was produced (51). The average sizes of the synthesized particles were 1.7 ± 0.2, 1.8 ± 0.5, 1.6 ± 0.5 nm in three different buffers respectively. The synthesis of spherical and highly crystalline Pt NPs of size 2.2 nm was synthesized using honey at 100°C in 4 h and it was observed that increase in reaction time leads to the formation of nanowires. N. Gupta *et. al.*, (53) described the green aqueous synthesis of spherical Pt NPs having an average diameter of 10 nm using tannic acid at room temperature within 5 min and so synthesized Pt NPs were used as catalyst for degradation of dye. Polyoxometalates as both reducing and bridging molecules was used in the synthesis of Pt NPs decorated carbon nanotubes at room temperature within 5 min with an average diameter of 2.5 ± 0.5 nm (54). One-pot template-free synthesis of three-dimensional Pt nano flowers with uniform size of 30 nm using green solvent, ethanol as the reductant and graphene oxide (GO) nanosheets as the stabilizing material by vigorous stirring of the mixture at 30°C for 1h was achieved by Xiaomei Chen *et. al.*, (55). Duangta Tongsakul *et. al.*, (56) has synthesized hydrotalcite-supported Pt NPs by immobilization method using soluble starch as a reducing and stabilizing agent under vigorous stirring at neutral pH at 373K for 1 h. Also uniform spherical Pt NPs of size ranging from 2-4 nm were obtained within 5 min using starch as the reducing and stabilizing (57). It shows that the reduction efficiency of starch is more in alkaline conditions. Synthesis of uniform Pt NPs with diameters of 13 ± 5 nm is possible using water as a solvent (58) when the reaction was carried out in a stainless steel Teflon lined metallic bomb inside a preheated box furnace at 190°C for 6 h. Irregular-shaped Pt NPs of size ranging from 2-5 nm by stirring (750 rpm) H_2PtCl_6 and trisodium citrate at 100°C for 90 min is carried out elsewhere (59).

Biological synthesis

Biological synthesis of metal NPs is advantageous over other conventional methods (chemical and physical methods), because biological routes involve the use of natural sources such as different prokaryotic and eukaryotic organisms which is mostly comprises of different bacteria, fungi, plants etc. (Figure 3). Since NPs are obtained from the natural reducing agents such as phytochemicals, proteins and vitamins present in microbes and plants make the synthesis procedure cost effective and also abolish the need to use harsh chemicals which reacts with nanomaterials making them toxic. Biological methods in turn termed as green synthesis have been widely employed in the field of nanotechnology and nanobiotechnology in the past decade by researchers to obtain different metal NPs. Very few reports available on the biological synthesis of Pt NPs which are discussed below.

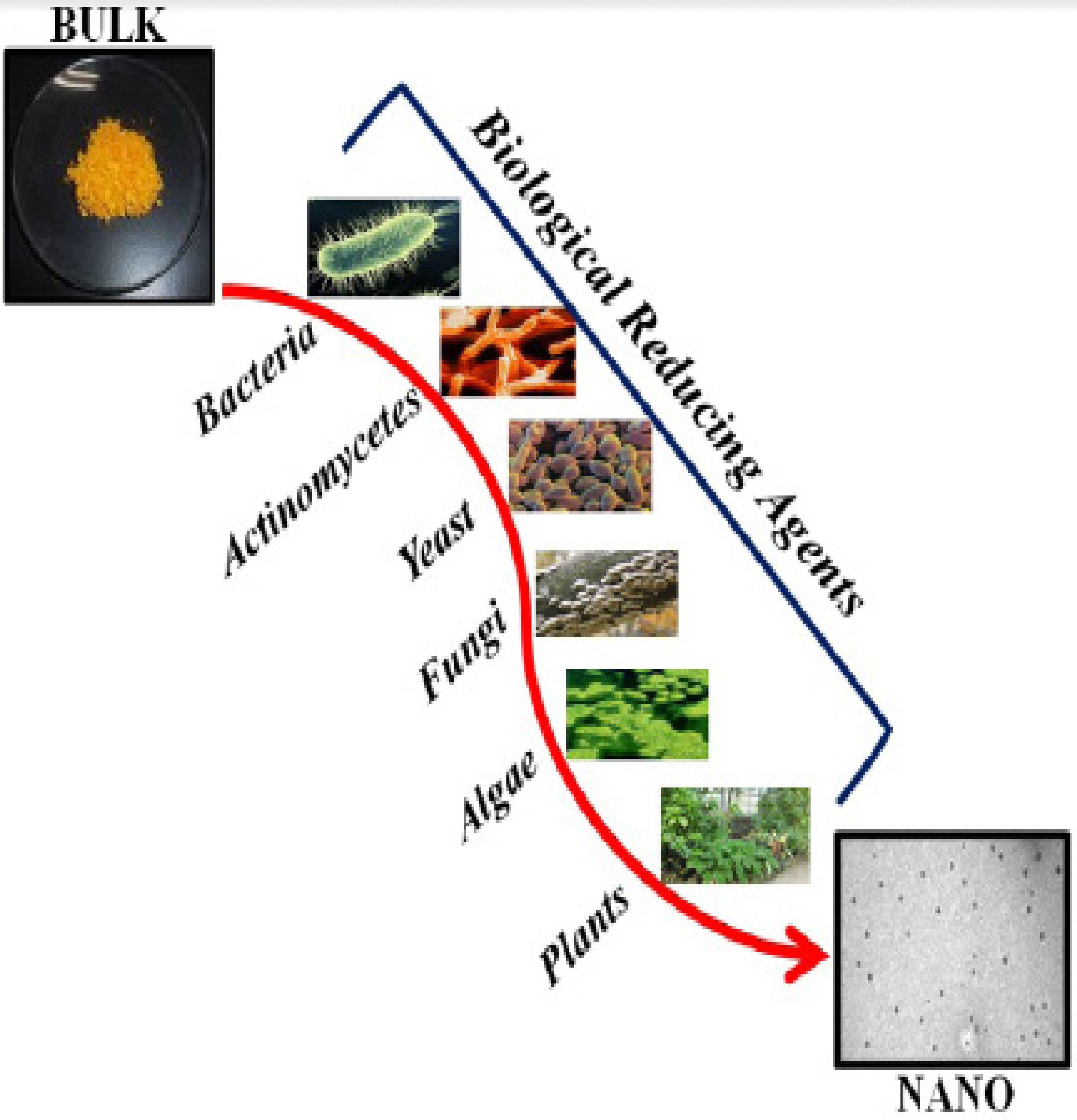


Figure 3: Biological reducing agents used in green synthesis.

Synthesis of Pt NPs using microorganisms

Various prokaryotic and eukaryotic microorganisms are used in the synthesis of metal NPs. Bacteria being the most copious prokaryotic microorganisms on the earth, they are greatly diversified in size and shape, and their ability to live in all kinds of habitats, extremely high or low temperatures, acidity, alkalinity, and salt or sulfur concentrations whereas fungi are eukaryotic organisms that live in a wide variety of natural habitats. They are mostly decomposer organisms, and more than 70,000 species have been described out of an estimated total of 1.5

million species. These organisms possess the ability to digest food extracellularly, secreting special enzymes to hydrolyze complex compounds into simpler molecules, which are then absorbed and used as an energy source. Synthesis of Pt NPs using microorganisms mainly includes used of bacteria and fungi (Table 2). Lengke et al has reported synthesis of spherical Pt NPs at 180°C using *Plectonema boryanum* (60). Anisotropic Pt NPs with the particle size ranging from 10-50 nm was obtained under ambient condition using *Fusarium oxysporum* (61). Synthesis of Pt NPs is done using marine bacteria *Shewanella algae* at 25°C and neutral pH within 60 min (62). The lactate which is present in the organism *S. algae* acts as electron donor and helps in the reduction of $PtCl_6^{2-}$ ions (62). Also, sulphate reducing bacteria can reduce Pt(IV) to Pt and pH plays an active role in the reduction process (63). The hydrogenase enzyme from the *Fusarium oxysporum* can produce Pt NPs (64) and the bioreduction of H_2PtCl_6 occurs on the enzyme at a site that is remote to the active site whereas reduction of $PtCl_2$ occurs through an active enzymatic process on the same enzyme (65). Further cell free extract of sulphate reducing bacteria also was used to synthesis of rectangular Pt NPs with size ranging from 50–300 nm under dark condition at 65°C (65). Pt NPs of size ranging from 5-30 nm was synthesized under ambient conditions using *Fusarium oxysporum*, time required for the formation of NPs was 96 hours which is too long. Natural proteins secreted by the fungus can be used as capping agent for NPs (66). *Neurospora crassa* can synthesize spherical Pt NPs under ambient conditions in 24h with the size ranging from 4-35 nm and presence of Pt NPs on the cell wall and cytoplasm was also detected during the study using thin section analysis (67).

Table 2: Synthesis of Pt NPs using microorganisms

Sl. No	microorganism	Name of the species	Size	Reference
1	Bacteria	*Plectonema boryanum*	10-50 nm	60
2	Bacteria	sulphate reducing bacteria	-	63
3	Bacteria	sulphate reducing bacteria	50-300 nm	65
4	Algae	*Shewanella algae*	~5 nm	62
5	Fungi	*Fusarium oxysporum*	10-50 nm	61
6	Fungi	*Fusarium oxysporum*	100-180 nm	64
7	Fungi	*Fusarium oxysporum*	5-30 nm	66
8	Fungi	*Neurospora crassa*	4-35 nm	67

Synthesis of Pt NPs using plant extracts

Using plant extracts for the synthesis of metal NPs has been widely employed because of its simplicity, less time consuming and non toxic nature. Various factors play vital role in the production of NPs and tuning their properties using plant extracts, major factors such as concentration of plant extract, nature of extract, concentration of metal salt, pH, temperature and reaction time. Very few reports available on the plant mediated synthesis of Pt NPs compared to Ag and Au NPs (Table 3). Green synthesis of Pt NPs is reported using *Diospyros kaki* extract (68). The average size of synthesized NPs is found to be 5 nm at 95°C which is not usually observed in synthesis of other nobel metal nanoparticles. *Cochlospermum gossypium* mediated synthesis of Pt NPs using autoclave at 15 Psi (120°C) are crystalline with average particle size of 2.4 ± 0.7 nm which is stable for 6 months (69). Jiahui Kou *et. al.,* (70) used beet juice to synthesize Pt NPs using microwave (100°C/280 Psi) and synthesized nanoparticles were spherical in nature with average size of 3 nm whereas irregular shaped Pt NPs was obtained using *Ocimum* sanctum leaf extract at 100°C in 1h (71), but aggregation of NPs happened due to high temperature. The synthesized Pt NPs was spherical with average size of 2.4±0.8 nm using *Cacumen Platycladi* extract (70% of the extract concentration) after 24h of reaction time (95.9% conversion) at 90°C. The presence of proteins and flavonoids in the extract are responsible for the reduction of platinum ions to Pt NPs. Recently Mohan Kumar *et. al.,* (73) used *Terminalia chebula* seed extract to produce spherical Pt NPs with average size of 4 nm at 100° C within 10 min. Using HPLC and FTIR data authors also suggested the possible reducing and stabilizing mechanism.

Table 3: Synthesis of Pt NPs using plant extracts.

Sl. No	Plant	Part used	Reaction condition	Morphology and size	Reference
1	Diospyros kaki	Leaf	95° C	Anisotropy 5 nm	68
2	cochlospermum gossypium	Gum	15 Psi, 120° C	Spherical 2.4 nm	69
3	Beta vulgaris	Beet juice	280 Psi, 100° C	Spherical 3 nm	70
4	Ocimum sanctum	Leaf	100° C, 1 h	Anisotropy 3 nm	71
5	*Cacumen Platycladi*		92° C, 24 h	Spherical 2.4 nm	72
6	*Terminalia chebula*	seed	100° C, 10 min	Spherical 4 nm	73

Mechanism involved in the green synthesis of Pt NPs using microorganisms and plants

Mechanism involved in the green synthesis of Pt NPs has been not explored in the literature. Understanding the mechanism involved in reduction and stabilization of metal NPs by green synthesis using plant extracts and microorganisms is an interesting area in green synthesis. Though lot of works has been done on the green synthesis of noble metals such as Ag and Au using plants and microbes, complete mechanism involved in reduction and stabilization has yet to be explored. Since green process involves the use of single regent which is multifunctional (reducing/stabilizing) in nature understanding its dual role at the same time is very interesting. Various researchers have been proposed mechanisms based on their understanding. On the basis of these reports we propose general scheme involved in the green synthesis of metal NPs (Figure 3). Synthesis and stabilization of metal NPs using microorganisms is interesting and it has been postulated that reduction of metal ions to their nano forms occurs due to the proteins secreted by these organisms (74). The amino acid residues in the proteins secreted by microorganisms play important role in the synthesis and stabilization of NPs. Due to less number of reports which explains the mechanism of microbial meditated synthesis of Pt NPs, the mechanistic aspects need to be studied in depth. Plant mediated synthesis has become common field in NPs synthesis because of its simplicity, which includes single step reaction to obtain stable NPs. The mechanism involved in this process has been explained by various groups during the synthesis of different metal NPs. General procedure involves that the plant phytochemicals such as phenols, tannins, alkaloids and flavonoids etc. take part in the reduction of metal ion to its nano form; further oxidized form of the phytochemicals will take part in the stabilization by capping onto the surface. The reduction of metal occurs due to the involvement of hydroxyl groups present in the polyphenols and the polyphenols undergo oxidation to form their respective quinine forms where carbonyl groups in the oxidized polyphenols helps in stabilization by coordinating with NPs by electrostatic interaction. Recently based on hard-soft acid base (HSAB) principle Mohan Kumar et al also explained that hard ligands come in contact with soft metal, resulting soft metal ion undergoes reduction because complexation is not preferential, whereas at the same time hard ligands undergoes oxidation to form soft ligands, which in turn makes coordination with formed NPs and makes them stable by preventing aggregation (73).

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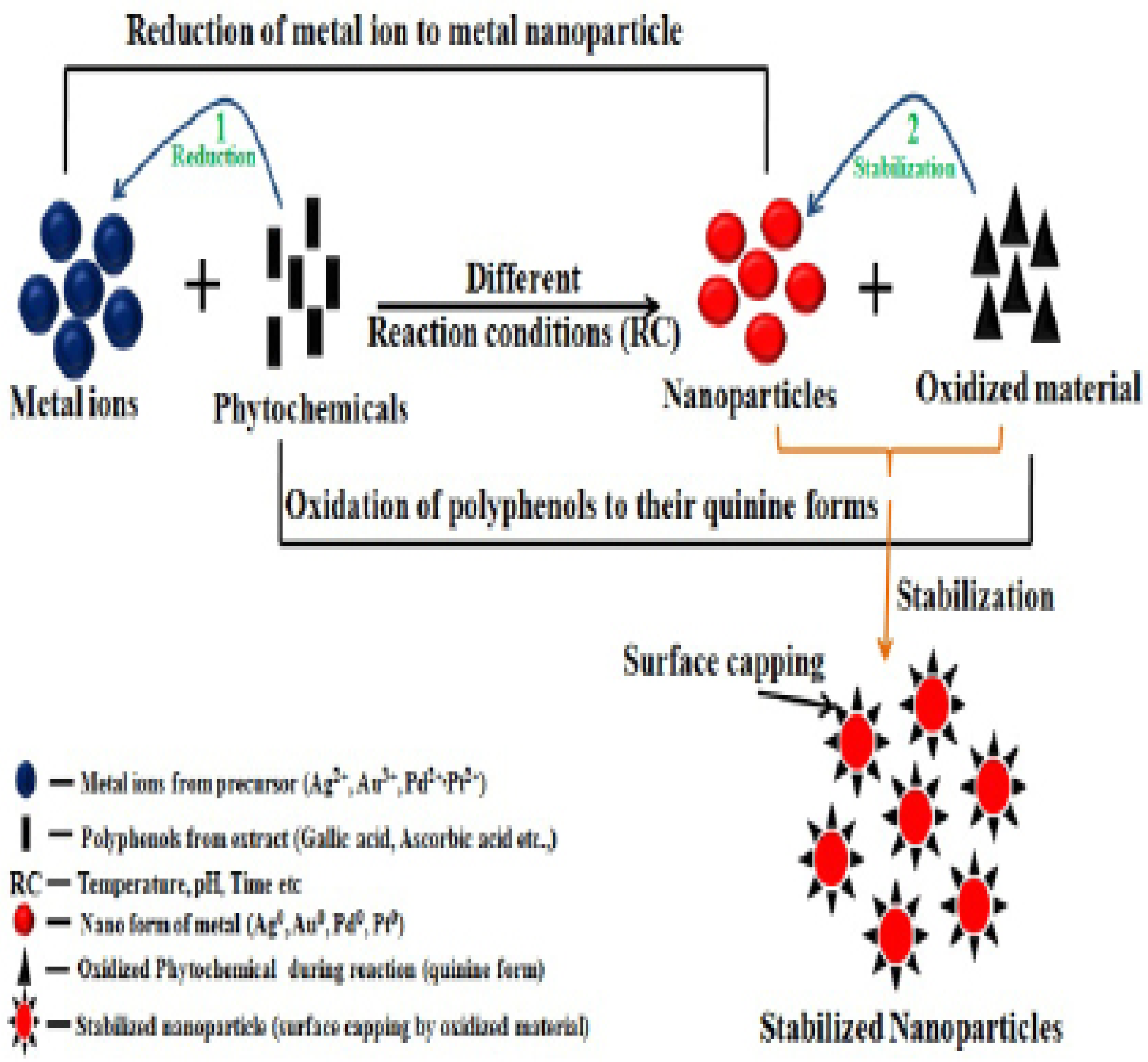
Reduction of metal ion to metal nanoparticle
1
Reduction
2
Stabilization
+
Different
Reaction conditions (RC)
+
Metal ions
Phytochemicals
Nanoparticles
Oxidized material
Oxidation of polyphenols to their quinine forms
Stabilization
Surface capping
— Metal ions from precursor (Ag2+, Au3+, Pd2+, Pt2+)
— Polyphenols from extract (Gallic acid, Ascorbic acid etc.,)
RC — Temperature, pH, Time etc
— Nano form of metal (Ag0, Au0, Pd0, Pt0)
— Oxidized Phytochemical during reaction (quinine form)
— Stabilized nanoparticle (surface capping by oxidized material)
Stabilized Nanoparticles

Figure 4: Possible mechanism involved in the reduction and stabilization of nanoparticles through biosynthesis

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CONCLUSION

Production of metal NPs using biological substances is an interesting and promising area in the nanotechnology research. Various biological entities have been exploited in the biosynthetic routes for synthesis of metal NPs. Nanomaterials of Ag, Au, Pd and Pt have been reported till date using different prokaryotic and eukaryotic organisms, among these biological forms phototrophic eukaryotes such as plants are regarded as potential and renewable nanofactories for the biological synthesis because of their simplicity and eco-friendly nature. Large scale production of different metal NPs using biological entities is still not under progress though this route eliminates toxic chemicals and also makes the procedures simple, scientists should focus on this particular issue to make biological synthesis as alternative to conventional methods in large scale industrial productions. Fabrication of Pt NPs using natural reducing agents is little difficult compare to other noble metals due to its low reduction potential and need of additional concerns such as temperature, concentration and pH etc. Considerable efforts have been put forward to synthesis Pt NPs using both microorganisms and plants, researchers successfully have reported the synthesis of Pt NPs with different sizes, shapes and morphologies followed by their applications in certain areas. Most of the reports conclude the dual role of reducing agents used in synthesis; hence understanding the mechanism involved in reduction and stabilization in single step without adding additional reagents will be interesting which has to be studied in depth. Synthesis of Pt NPs by renewable and biocompatible agents with exclusive chemical, optical, electrical and physical properties are of great importance for wider applications in the areas of chemistry, electronics, medicine and agriculture. Overall, the green synthesis is an exciting area in nanotechnology which makes significant impact on future advancements in various disciplines.

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Low-cost and eco-friendly green methods for graphene synthesis

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Abstract

Graphene, a god's material, exhibits the outstanding properties which promise different applications in biology, computers, electronics and other engineering, nanoscience and nanotechnology. Various chemical and physical methods have been established for the production of graphene from graphene oxide and graphite, each with their own disadvantages and advantages. However, the usages of this material in different applications greatly depend on their production scale, cost and dispersibility in different solvents. In this prospect, deoxygenation of graphene oxide is a versatile method to obtain a large scale graphene in low cost. Moreover, the development of eco-friendly methods would be an added advantage to obtain a biocompatible graphene with required surface functionalization. This review mainly emphases on a variety of low cost, green methods existing in the literature for the synthesis of graphene using plants, microorganisms, microwave and other green reducing agents. The promising advantages of the reported green methods and the possible future research directions also are discussed.

Key Words : Reduced Graphene Oxide, Green Synthesis, Functionalized Graphene.

Pages: 16 **References: 89**

INTRODUCTION

The development of techniques for synthesizing and characterizing novel class of materials in nanoscale is becoming of utmost significance in nanoscience and nanotechnology. This is in part due to the increasingly important role of nanoscale materials in current and future applications in different fields such as physical, chemical, biological engineering, and computer sciences (1). However, their unique and exceptional thermal, mechanical, electronic, and biological properties made them different from other macroscale materials (2). But still the fabrication of nanomaterials with required properties is a major continuing challenge within the field of nanotechnology.

Graphene, an isolated layer of carbon atoms from graphite, was first identified through the ground breaking experiments done in 2004 by Andre Geim and Konstantin Novoselov after peeling off graphite with an adhesive tape (3). Graphene has been considered as a super material, because of its outstanding physical properties. As a single atomic layer of graphite, it is the thinnest material (4) found with the young's modulus of 1 TPA (5) considered to be the strongest material found on the earth. Being a thin layer of carbon atoms, graphene also exhibits high conductivity due to high carrier mobilities and flexible properties which provides a tremendous scope of applications in the field of electronics (6). It also exhibits high specific surface area (2630 $m^2 g^{-1}$) (7) and is almost transparent, absorbing only 2.3 % of visible light (8). Perhaps the phenomenon exhibited by graphene such as balliastic transport and quantum hall effect, makes graphene to be considered in the perspective of physics (9). However, the conductivity properties will in turn depend on the thickness and the surface area of the graphene sheets (10,11). Hence, controlling the growth of graphene to obtain desirable properties is still remained as challenge.

These amazing features offer great potential applications in different fields such as nanoelectronics (12), composites (13), fuel cells (14), supercapacitor (15) as well as sensors (16) and catalysis (17). Despite the fact graphene is a potential candidate in electronic applications, research towards biological applications is still largely in the discovery stage and remains wide open. Nowadays, much attention is being drawn to the biological applications ranging from bioimaging (18), antimicrobial (19), drug delivery (20) and cancer therapy (21). The antimicrobial properties of graphene extend its applications to medicine, different industries, cosmetics, accessories, health and services (22).

However several methods have been reported for the synthesis of graphene using both bottom up and top down approaches (Fig. 1). High quality graphene have been produced by the bottom up methods such as the epitaxial growth on silicon carbide and the chemical vapour deposition, which are cost effective and the growth conditions of graphene is uncontrollable with poor uniformity (23,24). Moreover, the top down approaches includes the first method which was developed to isolate graphene experimentally is the micromechanical cleavage, where the scotch tape has been used to slash the layers of graphite apart. Although, the method has advantages over the production of high quality graphene, but the method is labour dependable and slow in process. Hence, this method is mostly restricted to study the fundamental features of graphene but not for the commercial applications (3).

Additionally, the electrochemical exfoliation and the solvent based exfoliation methods are found of using surfactants which prevents the agglomeration of the formed graphene sheets by attaching onto their surface, which in turn creating the effects on the electrical and electrochemical features of the graphene (25,26,27). Although the exfoliation of graphite intercalation compounds have been reported in the early 1916, the development of new solvent (NMP, Ethanol) and thermal based exfoliation of new graphite intercalation compounds have shaped the new area for the production of graphene. But, the usage of some compounds like iron chloride which decomposes at 100^{o}C and the ionic liquid crystals which further needs the mild heating conditions for their intercalation into the graphite and hence this method is restricted to use only at specific reaction conditions (28,29).

Another extensively used technique in the synthesis of few layered graphene includes the arc discharge method with the following demerits of using high voltage current requirement and the different buffer gases (30). Later, graphene have been also successfully obtained by the longitudinal unzipping of carbon nanotube by Prof. James M. Tour. However, this method suffers from the usage of strong oxidizing agents which in turn affect the electronic properties of graphene and also the evolution of harmful gases during the synthesis process causes the environmental related issues (31, 32).

Alternatively, the production of graphene from graphene oxide reduction is more promising method because of easy manipulation and transfer onto the substrate with large scale production, whereas the other methods are not suitable for bulk production of graphene. Numerous thermal and chemical methods have been developed for the production of graphene from graphene oxide. However, the usage of toxic and hazardous chemicals for the reduction of graphene oxide made the synthesized graphene less promising towards the biological and human related applications. In addition, reduction of graphene oxide through thermal and chemical methods results in the formation of hydrophobic graphene, which further causes their irreversible agglomeration through their π-π interactions and in turn seriously obstruct their production, transfer and storage (33, 34).

Although the above mentioned methods have their own advantages and disadvantages over each other, the challenges remain for the controlled production of high quality graphene in bulk scale. Also, the problems with aggregation of sheets have to be solved with the surface functionalization which is also an important target to exploit its applications in various fields of science as the properties of graphene are associated with the individual sheets. However, the very recent advances show the important role of biosynthetic and microwave methods in the production of graphene. The use of green methods in this area is growing fastly due to the easy experimental steps and simultaneous surface modification during the synthesis process. Additionally, biological synthesis of graphene is an eco-friendly method without the use of hazardous, toxic and costly chemicals. For example, production of graphene by chemical method (e.g. hydrazine, sodium borohydride) may lead to adsorption of these toxic chemicals onto the surface of graphene sheets raising the new toxicity issue (33,34). Hence there is an increasing demand for new, eco-friendly and easily scalable chemical approaches for graphene synthesis. On the other hand, the use of plants, microorganisms and microwaves methods for green synthesis of graphene is still in early stages (Fig. 2). In addition, the biosynthesis of graphene is a green chemistry method without the use of harsh and toxic chemicals.

Towards Green synthetic methods of graphene synthesis

Our distinctive aim is the application of green chemistry principles to develop low cost, green and eco-friendly synthetic strategies for graphene synthesis by avoiding the use and generation of hazardous and poisonous chemicals. In the following sections we have discussed about different green methods developed for graphene production by using microwave methods, plant extracts, microorganisms, fungi, polyphenols, other natural biomolecules, and green reducing agents.

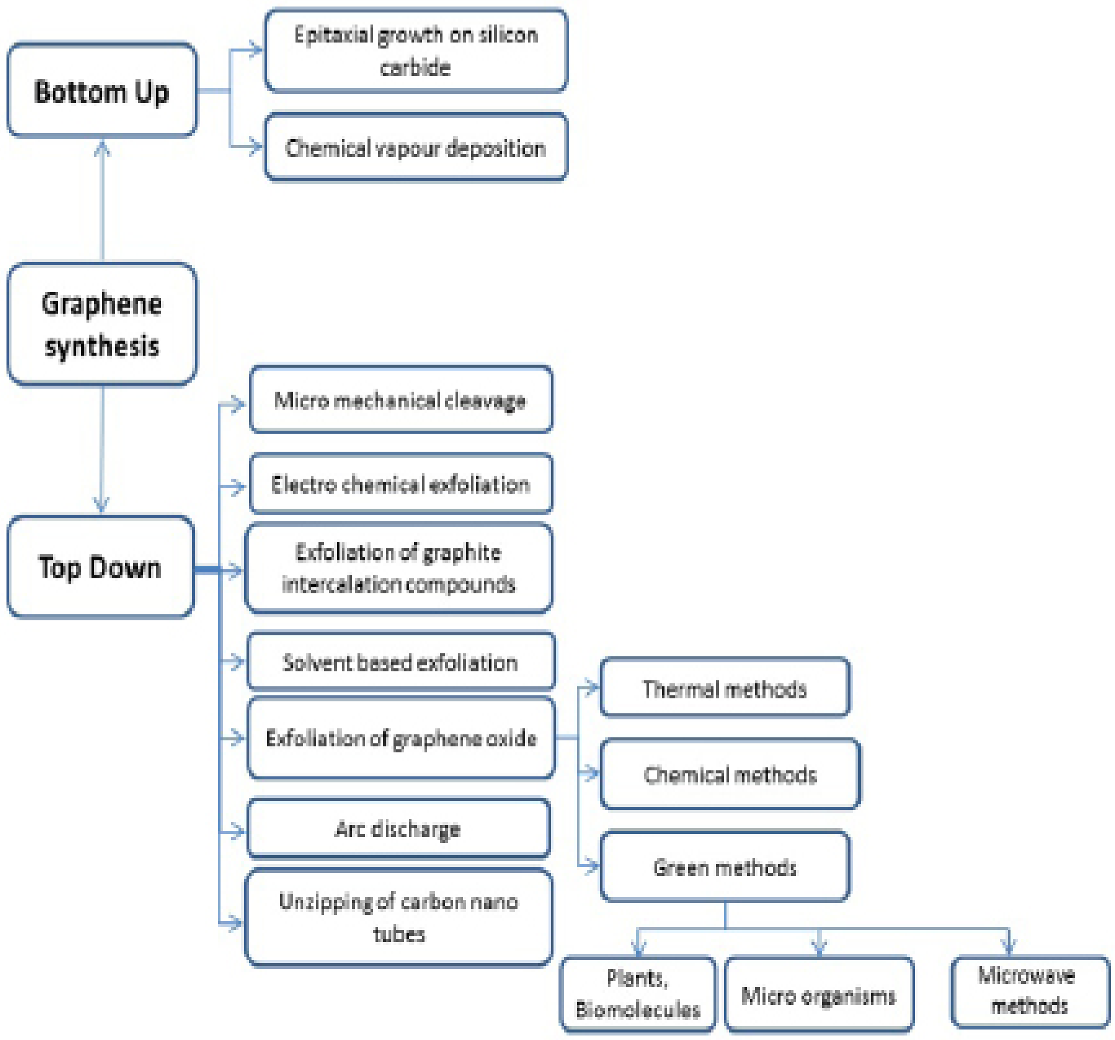
Bottom Up
Epitaxial growth on silicon carbide
Chemical vapour deposition
Graphene synthesis
Top Down
Micro mechanical cleavage
Electro chemical exfoliation
Exfoliation of graphite intercalation compounds
Solvent based exfoliation
Exfoliation of graphene oxide
Arc discharge
Unzipping of carbon nano tubes
Thermal methods
Chemical methods
Green methods
Plants, Biomolecules
Micro organisms
Microwave methods

Figure 1: Some important methods used in Graphene synthesis

Microwave methods

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Among all the above green methods, microwave energy methods are considered as the best alternative method for chemical reduction due to its environment friendliness, low cost and fast reaction time facilities. This method has several advantages over other methods: (i) the higher reaction rate (ii) selectivity (iii) very short realization of reactions. So far, several studies have reported on the synthesis of graphene by using microwave energy.

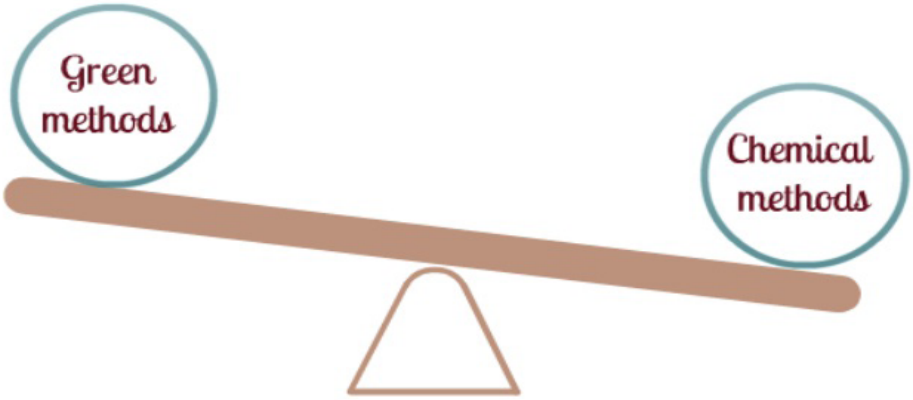

Figure 2: A comparison of synthetic strategies developed for graphene synthesis using green and chemical methods

Microwave irradiation methods (MWI) have been established for the production of many different nanomaterials with the regulated size and shape without using high temperature and pressure (35). However, the structure and composition of carbon materials play main role in their microwave absorption capability. For instance, Hu *et. al.,* used microwave heating for the preparation of super capacitor graphene material from graphite oxide (36). Authors also have studied the microwave absorption capability of graphene based materials by varying the oxygen content in graphite oxide, where the increase in the oxygen content of graphene oxide decreases the microwave absorption capacity and vice versa, which interns all these phenomena depends on the π-π conjugated structure in the materials (36). Sridhar *et. al.,* reported the production of graphene sheets in 90 seconds by irradiation of an ultrasonicated mixture of graphite flakes, ammonium peroxy disulfate and hydrogen peroxide to the microwaves at 500W (37). The study of morphology by Scanning electron microscopy (SEM) revealed that the pores of graphene worms are separated by homogenous distance, indicating the homogenous expansion of graphite along the c-axis. BET method confirmed the surface area (590 m^2/g) of graphene formed is lower than the theoretical value, due to the overlapping one by one and stacking of graphene layers formed. Raman spectra implied the formation of highly pure graphene with a lower limit of defects (37).

Zhu *et. al.,* reported the instantaneous exfoliation and reduction of graphite oxide by quick microwave exposure. Transmission electron microscopy (TEM) images, showed wrinkled and folded regions on graphene sheets and an irregularly stacked layers on the edges. Graphene produced is having lower defects with high surface area and conductivity making it as promising material to use in ultracapacitors (38). Similarly, Li *et. al.,* have made a rapid and ultra-fast (<5 seconds) method for large scale graphene synthesis by the irradiation of microwaves onto graphite oxide. Graphite oxide can strongly absorb the microwaves and causes an ultrafast raise in the temperature, which finally results in the reduction of graphite oxide to graphene without the use of any external reductant (39). Shen *et. al.,* synthesized graphene in one step by microwave irradiation of graphite oxide and ammonium bicarbonate mixture. TEM images indicate homogeneous, smooth flake like shapes of graphene sheets resembling the silk veil waves with less aggregation (40). In the same way, Janowska et al. developed a low temperature route for the first time to synthesize large size aqueous stable graphene sheets of few layers using the microwaves irradiation of expanded graphite in water and ammonia. TEM and electron diffraction analysis revealed that the exfoliated product contains mono, bi, and few-layer graphene sheets with relatively straight edges (41).

Microorganisms

Sustainable routes to graphene synthesis in greener fashion also involved the use of microorganisms (42-49). The main advantages of these methods include simple operations, low cost, and green scalable ways. Many microorganisms including bacteria and yeast have been found to be adept of synthesizing graphene.

Salas *et. al.,* determined the capability of environmental bacteria such as *Shewanella species* to process the synthesis of graphene under anaerobic conditions. Carbon percentage from X-ray photo electron spectroscopy (XPS) results of both Shewanella and chemically reduced graphene proved the reducing ability of bacteria. Also the conductivity properties of bacterial graphene are in equivalence with that of chemically produced graphene resulting an ease method towards the electronics related applications (42). Later, Wang *et. al.,* demonstrated that anaerobic conditions are not necessary for microbial reduction of GO by *Shewanella.* Graphene oxide reduction involves participation of electron mediators and proceeds via the direct electron transfer. The produced graphene revealed similar electrochemical, spectral and structural properties to the chemically converted graphene (43). Analogously, Akhavan *et. al.,* have studied the use of *Escherichia coli* (*E. coli*) bacteria to reduce graphene oxide and also proved the antibacterial activity of the graphene formed (44). However, Gurunathan *et. al.,* has reported for the first time the formation of water dispersible graphene in bulk scale by an environment friendly approach, using *E. coli* bacteria as reductant (45). Authors have also reported the usage of *Pseudomonas aeruginosa* biomass for the production of graphene and studied its biocompatibility towards mouse embryonic fibroblast cells (46). Likewise, Tanizawa *et. al.,* have used microorganisms extracted from river side water for the production of high quality graphene from graphene oxide (47). On the other hand, Yuan *et. al.,* fabricated a single step mediated graphene-bacterial network onto the anode surface, involving the addition of graphene oxide and acetate into a microbial fuel cell. The obtained material showed the comparable conductivity to that of chemically reduced graphene (48).

In contrast of using bacteria for graphene synthesis, Khanra *et. al.,* developed a new route for the instantaneous reduction of graphene oxide by using yeast as a biocatalyst, which is cheap, biocompatible and easily available. It is proposed that the amine functionality of nicotinamide adenine dinucleotide phosphate (NA-

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DPH), present in the yeast can proficiently reduce the graphene oxide. Also, the adsorption of NADPH onto the surface of graphene is confirmed by Raman, Fourier transform infrared spectroscopy (FT-IR) and XPS analysis (49).

Polyphenols and Plant Extracts

The sustainable synthetic route for the production of graphene involves alternative sources by reducing or avoiding the use and generation of toxic chemical substance. Polyphenols, which acts as both reducing and stabilizing agents, offer very simple, green synthetic route for the synthesis of highly water dispersible graphene. For instance, Xiao and Li *et. al.,* reported the highly dispersible reduced graphene oxide molecules (1.2 mg/ml in water and 4 mg/ml in dimethyl sulfoxide) by using gallic acid as reducing and stabilizing agent, both at room and high temperature conditions. The average thickness and the conductivity of graphene synthesized at high temperature medium is less compared to the one synthesized at room temperature, indicating the presence of less number of stabilizing molecules onto the surface of graphene synthesized at higher temperature (50).

Further, Lei *et. al.,* have shown the formation of graphene by using tannic acid as reducing and stabilizing agent. AFM analysis revealed that the average thickness of graphene sheets was about 1.5 nm with a single layer of tannic acid molecules adsorbed on their surface preventing the agglomeration of the sheets. The authors believed that the removal of hydroxyl and epoxy groups in GO have been carried out via a two-step SN_2 nucleophilic reactions followed by elimination reaction. The process results in the release of water molecule and would convert the tannic acid into its oxidized form (51).

On the other hand, plant based materials are getting more attention as the ideal candidates for the economic and large scale synthesis of graphene. Important parts of the plants such as seed, root, fruit pericarp, fruit juice, latex and stem cab are used for the synthesis of graphene. Polyphenols are being the active components, play important role in some of these syntheses (50-56). For instance, aqueous extracts of all the plant parts contain high amounts of polyphenols (52). Based on this concept, Thakur *et. al.,* have reported the synthesis of highly conductive graphene with large specific capacitance, using the leaf extracts of *Mesua ferrea Linn., Colocasia esculenta* and a peel extract of *Citrus sinensis*. The leaf and peel extracts of these plants contain easily oxidizable flavone, flavanoids, pectins, apigenin, ascorbic acid, luteolin which are involved in the reduction of graphene oxide. TEM images showed a silk like outward show of graphene after reduction. FTIR spectrum confirmed the comparable efficiency of plant extracts for the GO reduction to that of hydrazine [53]. Similarly, the dried leaf extracts of *Potamogeton pectinatus L., Ceratophyllum demersum L., Lemna gibba,* and *Cyperus difformis,* were used for the synthesis of highly water dispersible graphene. The ID/IG ratio of graphene obtained by this method almost matches with that of solvothermal method, indicating the production of high quality graphene compared to the chemical method (54). Gurunathan *et. al.,* have used the spinach leaves for deoxygenation of graphene oxide, resulting in water dispersible graphene with biocompatibility towards primary mouse embryonic fibroblast cells (55). Authors have also used *Ginkgo biloba* extract for the synthesis of stable water dispersible graphene and studied its biocompatibility towards the MDA-MB-231 human breast cancer cells, opening potential biological applications such as stem cell growth, tissue engineering, molecular imaging, biosensing and other drug delivery applications for carrying anti-inflammatory, water insoluble anti-cancer drugs (56).

In another study, Kuila *et. al.,* demonstrated the comparable efficiency of wild carrot root to that of hydrazine for the room temperature reduction of graphene oxide (GO) synthesis. The small angle electron diffraction pattern obtained from TEM images and FTIR studies revealed the possibility of adsorption of beta-carotene onto the surface of the formed few layered graphene sheets (57). In the same way, Shi and Wang *et. al.,* have used green tea solution to produce graphene. Formed graphene showed a stable and good dispersibility in low boiling point solvents (ethanol, acetone) due to the surface adsorbed polyphenols which favored the applications towards the composites and device preparation. However, the adsorbed tea polyphenols has shown negative effect on the conductivity of the formed graphene, confirmed by the comparing with the conductivity of graphene formed by using hydrazine, other green and chemical reducing agents (58).

In addition, few reports are available by using natural carbon sources as a precursor for graphene synthesis. For example, Kalita *et. al.,* used a solid botanical camphour for the synthesis of mono and bilayered graphene by controlled pyrolysis, leaving its scope of applications to electronics. The synthesized graphene sheet had transmittance of 91% and resistance of 860 O/sq (59). In the same way, Ray *et. al.,* showed a simple method of high quality graphene synthesis, by heating the original petals of lotus and hibiscus flowers at different temperature conditions under argon atmosphere. The selected area electron diffraction (SAED) pattern and TEM microscopic analysis of graphene showed the crystallinity with typical hexagonal symmetry and the best quality product is obtained at 1600^{o}C, compared to the lower temperatures, due to the significant removal of oxygen containing groups at higher temperatures (60). Very recently, Lee *et. al.,* have studied the comparative reducing efficiency of seven plant extracts towards the deoxygenation of graphene oxide (61).

Other natural biomolecules and green methods

Current research in bio-synthesis of graphene using environmentally friendly reductants has opened a new era in rapid and safer methods for production of graphene. The first example of use of eco-friendly reducing agent used for the reduction of graphene oxide was Vitamin C (62-64). Gao *et. al.,* has introduced a new, green method to produce dispersed graphene solution that involved the use of vitamin C as the reductant and L-tryptophan as the stabilizer. Raman spectra analysis revealed more value of the D/G band ratio for synthesized graphene than graphene oxide used, suggesting the formation of more sp^2 domains during the reduction. The produced graphene is biocompatible, and 106 times more conductive than the graphite oxide used, resulting the usage of the obtained product in future biosensors and bioelectronics applications (62). During the same period of time, another group from United Kingdom used L-Ascorbic acid as reductant, for the room temperature reduction of graphene oxide in water. Oxidized products of L-Ascorbic acid acted as a stabilizer for the formed graphene to prevent the agglomeration by making it stable in aqueous media. Atomic force microscopy (AFM) analysis showed the thickness of formed graphene sheets is about 1.2 nm, which agrees well with the previous reported hydrazine reduced graphene (63). Similar work has been done by Fernandez-Merino et al. and their UV-Visible studies have proved the proficiency of L-ascorbic acid as green reductant to replace toxic chemicals like hydrazine. Graphene produced by this mode is soluble in water and other organic solvents such as dimethyl formamide and N-methyl pyrrolidine (64).

It is interesting to note that some of the sugars and proteins can function as reductants for graphene synthesis in aqueous media. Zhu *et. al.,* investigated the one pot synthesis of water soluble graphene nanosheets by using saccharides such as glucose, fructose and sucrose, for the reduction of exfoliated graphite oxide. Conductivity experiments have showed the good electrochemical properties of the graphene obtained. AFM analysis has confirmed that the capping agent is responsible for the increase in the thickness of the formed graphene nanosheets. Authors also investigated that reducing capability of sucrose is weaker than the individual glucose and Fructose (65). Kurasch and Li *et. al.,* have used glucose to produce highly conductive reduced graphene oxide (66). Similarly, Akhavan *et. al.,* prepared the biocompatible reduced graphene oxide in the presence of Fe catalyst by using glucose as reductant and stabilizing agent. Graphene obtained exhibits a competent NIR photothermal therapeutic property (due to surface gluconate ions present on sheets) with that of single walled and multi walled carbon nanotubes, opening its applications in near future nanotechnology based cancer therapies (67). Likewise, Li and Wang *et. al.,* used monosaccharide medicine glucosamine as reducing agent for the reduction of graphene oxide (68). Same way, biocompatible graphene has also been produced using starch as reducing and stabilizing agent (69). Huang and Wang *et. al.,* showed the synthesis by taking heparin as green reducing agent to synthesize aqueous stable graphene with very good biocompatibility and anticoagulant activity (70).

Pham *et. al.,* has presented a study of graphene synthesis by green reduction of graphene oxide using glutathione, and the formed graphene looks like rippled silk waves with an average thickness of 8 nm, which is larger than the previous reports published (71). Presence of capping agent may be the reason for the higher thickness of reduced graphene oxide sheets. Graphene also formed the stable dispersion in dimethyl sulfoxide, distilled water, and the agglomeration is prevented by the formation of hydrogen bonding between oxygen functionalities of graphene oxide and the oxidized forms of glutathione (71). Chen *et. al.,* reported the formation of uniformly dispersed graphene with the reduction of graphene oxide by using amino acid L-cysteine as both reductant and stabilizer. TEM microscopic analysis has showed the wrinkled paper-like graphene with sharp polycrystalline ring pattern, indicating the missing in the ordering between the graphene nanosheets (72). Analogously, Bose et al. have used glycine for the production of functionalized graphene with excellent aqueous dispersibility. Selected area electron diffraction (SAED) pattern showed the sharp diffraction dots indicating the highly crystalline nature of graphene formed. XPS N1s spectrum has shown the existence of nitrogen on the surface of graphene indicating the surface functionalization of graphene with glycine (73).

Liu *et. al.*, developed a green and facile route for the synthesis of graphene from graphene oxide by using gelatin as reducing and fictionalization agent. The formed graphene is highly soluble in water and other physiological fluids. Due to the high surface area and strong π-π conjugation, graphene got prominence role in drug delivery and cellular imaging with very good biocompatibility (74). Gurunathan *et. al.,* have proved humanin, a human polypeptide as alternate to the hydrazine as reducing agent for the production of graphene from graphene oxide (75). Deng and Liu *et. al.*, reported the one step synthesis of graphene oxide and protein-conjugated graphene oxide nanosheets by using Bovine serum albumin (BSA) as reductant. The BSA's reducing capability depends on pH and the ionization of phenolic groups present in Tyrosine residues, by which electron transfer takes place to graphene oxide and immediate transformation into quinine groups (76). However, very recently we have reported the naturally occurring milk protein, casein as green reducing agent for reduction of graphene oxide and subsequent decoration on the surface of graphene sheets. FT-IR, TEM and High performance liquid chromatography analysis have confirmed that the graphene obtained was surface modified with casein molecules. Carboxylic groups of casein molecules present on the surface of graphene are responsible for preventing the agglomeration of the formed graphene sheets (77). Hence, it is easy to prepare surface functionalized reduced graphene oxide with green reducing agents to obtain specific properties such as biocompatibility, dispersibility in various solvents to open up application in electronics, nanocomposites and other biological and environmental applications. However, the reduction and capping of graphene with various green reducing agents is schematically represented in figure 3.

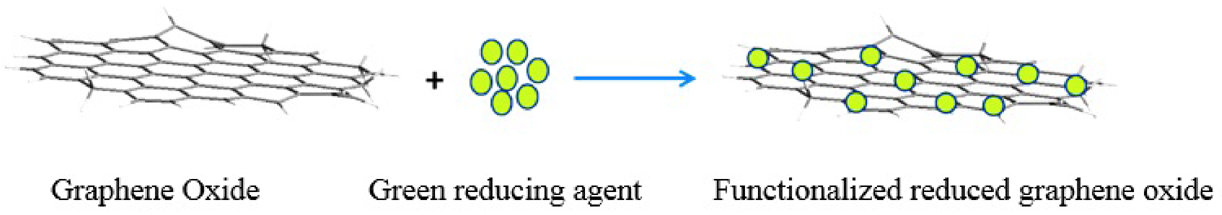

Figure 3: Schematic representation of synthesis of functionalized graphene with green reducing agents

In contrast to these, Esfandiar *et. al.,* showed the ability of melatonin as a powerful antioxidant and reductant for graphene synthesis. AFM images confirmed the thickness of graphene was 1.8nm, which revealed that the oxidized melatonin molecules adsorbed onto the surface of formed graphene sheets. Though these attached molecules result in reduction of electrical conductivity of graphene sheets, the prevention of agglomeration of graphene sheets was occurred for long time, when compared to the hydrazine reduced graphene, where the immediate agglomeration took place under UV irradiation (78). Kaminska *et. al.,* studied the ability of dopamine to effectively reduce the graphene oxide under sonication at room temperature and its substantial fictionalization (79).

Shen *et. al.,* showed eco-friendly reagents such as hexamethylenetetramine (HMTA) for the reduction of graphene oxide. The obtained graphene is highly dispersible in water (0.65 mg/mL) with long term stability than the previous reports. AFM images showed that the thickness of sheets was 1.28nm which was larger than the previous report, due to the capping reagent of HMTA used for reduction (80). Similarly, water dispersible graphene has also been synthesized by Gurunathan *et. al.,* using triethylamine as reducing, stabilizing agent and its biocompatibility was further confirmed by cell viability assays, leaving its scope of applications towards stem cells and other bio-applications (81). Haghighi *et. al.,* have synthesized electrocatalytically active graphene by using rose water as deoxygenating agent, presenting the scope of the material for biosensor preparations (82).

Huang and Liu *et. al.,* developed a green method to synthesize graphene by reduction of graphene oxide using zinc powder under acidic conditions at room temperature. TEM morphology images revealed the typical transparent and rippled silk like sheets in few layers. XPS data showed the maximum extent of removal of oxygen containing functional groups resulting in an increase in the conductivity of reduced graphene oxide 14 times higher than that of $NaBH_4$ reduced graphene oxide (83). Same work has been done by two other scientists: (i) Geng *et. al.,* reported highly conductive graphene with 70% transparency (84) and (ii) Mei *et. al.,* reported a rapid ultrasonication assisted room temperature synthesis of graphene by using the mixture of graphene oxide and zinc powder in acidic solution. One of the advantages of this method includes very fast reaction time of less than one minute, which is shorter than the other chemical methods reported (85). Hence graphene synthesized by this method has large scope of potential applications in the areas like photovoltaics, optoelectronics and electrochemistry by aiding as a flexible, ultrathin and transparent electrode material. Similarly, graphene was also produced by using aluminum powder (86) and iron powder (87), as reducing agents under acidic medium.

Perera *et. al.,* reported a green one pot hydrothermal synthesis of graphene from graphene oxide under strong alkaline conditions by adding NaOH. The formed graphene showed the similar properties to the graphene obtained by reduction with hydrazine (88). Zhang *et. al.,* the first time reported the use of polyelectrolyte as both reducing and stabilizing agent for graphene nanosheets synthesis. TEM morphology exhibits a thin wrinkle-like sheet, and the related selected area electron diffraction image showed the well-defined six-fold-symmetry patterns (89).

Future perspective

Several chemical, physical and biosynthetic methods have been reported so far for the synthesis of graphene. Most of these methods are still in the development stage and the main challenge is to obtain a highly pure and dispersive reduced graphene oxide without using any hazardous chemicals.

In the previous sections, we have discussed different eco-friendly and green routes that have been developed towards the production of graphene from graphene oxide. These methods are possessing several advantages including (i) easy, low cost production; (ii) usefulness and processability of material in different solvents; (iii) bulk scale production; (iv) avoiding the use and production of toxic substances. All these advantages can ultimately assist the use of graphene based materials in commercial applications.

It is seen that the reduced graphene oxide synthesized by using plant extracts and natural polyphenols is highly dispersible in both water and in some of the organic solvents, promoting its applications towards biological and energy related fields. These polyphenols did not only act as reducing agents, but also involved in the stabilization of the formed graphene making it highly dispersible by preventing the agglomeration of graphene sheets. However the ultra-fast production of highly dispersible graphene from plant extracts is highly desirable in future. On the other hand, the use of microwave methods for the reduction of graphene oxide, involves a unique advantage of rapid reaction times, when compared to other methods such as plant extracts and microbes.

However, some of the mechanisms of formation of graphene via green methods are not yet fully understood. Future work should involve the exploration of reduction performance of different biomolecules, optimization of reaction conditions involved in graphene synthesis and modeling the interactions between graphene oxide and the biomolecules will be helpful to upgrade the applications of graphene in several fields. The development of genetically engineered hybrid plants or organisms that can be able to produce higher amounts of biomolecules, enzymes required for graphene oxide reduction is highly desirable for rapid and bulk scale production of graphene.

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Green synthesis of reduced graphene oxide noble metal composites and their applications

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Abstract

Ĝraphene, two-dimensional carbon sheet with one atom thickness and single to several layered thinnest material in universe has created great research interest in many fields like physics, chemistry, material science, and biology. However, pure graphene sheets don't have wide scope of applications and they are restricted to very limited applications. Keeping this base point in mind, many efforts have been put forward for introducing secondary components or functional groups onto the graphene sheet, making these materials as graphene nanocomposites or hybrid materials. Now these materials can be used in day-to-day applications such as catalysts, energy storing devices, sensors, electrochemical and photochemical applications etc., due to the presence of various non-covalent forces such as hydrogen bonding, ionic, amphiphilic, and π-π interactions that are present between the graphene sheets and noble metal nanoparticles. Make these composites to be easily dispersed in various solvents, availability of high surface area and easy accessibility towards charge transfer nature are well developed in these composite materials. The graphene noble metal composite which they are prepared by greener method establishes non-covalent interaction rather than covalent interactions. The graphene nanocomposites act as promising electrode materials for oxygen reduction reactions (ORR), methanol oxidation reactions (MOR) as well as proton transfer membrane fuel cell technologies (PFMC). This review mainly focuses on synthesis techniques of graphene noble metal composites synthesized via greener approaches or techniques with a futuristic recommendation what are the remaining challenges that are to be fulfilled by the upcoming researchers.

Key Words : Graphene, Graphene Nanocomposites, Hybrid Materials, Greener Approach.

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INTRODUCTION

Nanotechnology is considered to be one of the major branches in science to the present research community which consists of different fields such as physical, chemical, biological and engineering sciences. This is the only field in which many novel techniques can be introduced or developed to probe and manipulate single atom and molecule with at least one dimension sized from 1 nm to 100 nm. It has brought a new enlightenment in many research fields such as fabrication of nanoparticles and incorporation of those onto single layered graphene sheets forming a nanocomposite material with advanced applications in different fields. With the invention of new analytical techniques such as TEM, AFM, DLS etc., the nanotechnology today has created a stage where it is considered to be the future to all technologies (1-4). Nanoparticles are of great scientific interest because they act as bridging substance between bulk materials and atomic or molecular structures. With improved properties of noble metal nanoparticles (NPs) such as gold, silver, platinum, palladium, etc, these NPs are to be thoroughly investigated further for broader scope of applications. The gold and silver metal NPs possess many of the enhanced photophysical properties such as absorption, scattering, fluorescence, surface-enhanced Raman scattering, and surface Plasmon resonance (SPR). Among all the above optical properties surface Plasmon resonance property can be seen in almost all the noble metal NPs. Some of the common applications of these noble metal NPs include electronics, photodynamic therapy, therapeutic agent delivery, sensors, probes, catalysis (5-7). Next to gold, silver is the second most noble metal which has special biomedical property such as anti-bactericidal nature and hence these noble metals are used in making biomedical materials. Other noble metals include platinum, palladium, osmium, iridium, etc, are employed as potential catalysts in hydrogenations, oxidations, and carbon-carbon bond formation, electrochemical reactions in fuel cells, hydrogen storage, and energy storage devices. The properties and applications of these noble metal NPs have extended to various fields. Also, incorporation of these noble metals on the graphene sheets open a new door step for development of new field of carbon family materials called as graphene noble metal composites. These graphene noble metal composites now possess the outstanding desirable properties within them. These properties cannot be attained or observed when they exist as individual materials. This review mainly focuses on synthetic techniques, properties and applications of graphene noble metal composites (GNMCs).

Graphene and graphene nanocomposites material

Graphene (G), a two-dimensional material (2D), composed of layers of carbon atoms packed into a honeycomb network, has become a promising material on the platform of material science in the last several years (8, 9). Even though GN is considered to be the mother of all graphitic forms, such as 0D fullerene, 1D carbon nanotubes (CNT) and 3D graphite, which have been extensively studied for decades, has not gained too much attention before the isolation of single-layer graphene sheets from bulk graphite in 2004 by two eminent scientists Geim and Novoselov at Manchester University which awarded the Nobel Prize in the year 2010 in Physics for their Ground-breaking contribution towards graphene materials (11-13). Due to the presence of π-conjugation in graphene moiety it exhibits remarkable unique properties such as high Young's modulus (~ 1.0 TPa) (14), large theoretical specific surface area (2630m^2 g^{-1}) (15), excellent thermal conductivity (~ 5000 W m^{-1} K^{-1}) (13), high mobility of charge carriers (200 000 cm^2 V^{-1} s^{-1}) (16) and high optical transmittance (~ 97.7%) (17), which make graphene to be an ideal building block in nanocomposites. Nanocomposites are also called as multiphase materials because normally they exhibit two phases such as one phase (dispersed phase) in the nanosize regime is dispersed in a second phase (matrix/continuous phase) resulting in a combination of the individual properties of the component materials. All of these properties make the emergence of novel nanocomposites. Graphene noble metal composites have been intensively developed, and found to exhibit a range of unique and useful properties, which are attracting more and more attention from the researchers. The main motivating forces that are mainly involved in the development of research on graphene based nanocomposites are the desire to combine the favourable properties of graphene with other nanomaterials, especially noble metals (18, 19). In this review we are mainly focusing on different greener methods of synthesis, uses of natural green reducing agents, microwave assisted method, solvothermal, hydrothermal, UV assisted method, photochemical, and electrochemical methods for the synthesis of reduced graphene oxide noble metal composites along with their real time applications in day-to-day life.

PREPARATION OF GRAPHENE FOR USE IN NANOCOMPOSITE MATERIALS

Preparation of graphene oxide (GO)

There are six widely used well-known methods for the preparation of graphene in large quantities in literatures. These methods are 1) micro-mechanical exfoliation method (20, 21), 2) chemical vapour deposition method (22, 23), 3) epitaxial growth (24-26), 4) longitudinal unzipping of CNTs (27-29), 5) organic synthesis routes (30, 31) and 6) colloidal suspensions from graphite and graphite derivatives (32-34). All these methods have their own advantages and disadvantages (35, 36); among these methods the colloidal suspension from graphite and graphite derivatives stands as a primary strategy for the production of graphene in larger quantities followed by chemically modified graphene (CMG) via chemical functionalization and used for wide range of applications (37). Among all the synthesized CMG, reduced graphene oxide (RGO) is the most common product obtained through graphite oxide exfoliation. Nowadays, most G-based nanocomposites are fabricated with graphite oxide as the starting material. Methods for the oxidation of graphite to graphite oxide include Brodie method (38), Staudenmaier method (39) and Hummers method (40).

Reduction of graphene oxide

Graphene oxide can be easily reduced into stable reduced graphene oxide (RGO) by using various reducing agents such as hydrazine monohydrate (41–43), sodium borohydride (44, 45), hydroquinone (46, 47), and strong alkali (48). Due to presence of highly toxic, environmentally harmful nature sometimes they act as explosive materials when used in larger quantities. To avoid these toxic and hazardous chemicals in chemical reduction scientists have invented greener reducing agents for reduction of graphene

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oxide which are eco-friendly, and fast.

Functionalization of graphene oxide

The reduction is a process where the oxygen functional groups are successfully removed from the graphene whereas functionalization of graphene stands for adding up of additional functional groups such as nanoparticles are loaded on the graphene sheets, which modify graphene sheets with desired properties for selective applications such as to increase the solubility of graphene in various solvents (49, 50) which improves the manipulation and processing ability of graphene sheets in the fabrication of various devices (51, 52). However, the functionalization of graphene is done by two methods i.e. covalent attachment or noncovalent adsorption of various functional molecules. Whenever we are utilizing green reducing agents for synthesis, they can functionalize the graphene sheet through noncovalent approach only rather than covalent approach. The noncovalent approach can be brought through hydrogen bonding, π-π stacking, electrostatic interactions, and van der Waals interactions. The main advantage of the noncovalent functionalization of graphene is that functional groups could be introduced into graphene without affecting its structure and electronic network, so that the novel properties of graphene are retained.

GREEN SYNTHESIS OF REDUCED GRAPHENE OXIDE NOBLE METAL COMPOSITES

Au NPs-reduced graphene oxide (Au NPs-RGO) nanocomposites

Xu *et. al.*, has proposed the synthesis of gold nanoparticles (Au NPs) / reduced graphene oxide composites by using eco-friendly biocompatible materials like regenerated silk fibroin as both reducing and stabilizing agent (53). The flowerlike Au NPs-RGO composite shows excellent catalytical activity for oxygen reduction reactions (ORR) compared to the branched and spherical Au NPs-RGO composites due to their high specific surface area and the presence of sharp edges or secondary asperities (i.e. tips) that provides active reaction sites for ORR (53). Iliut *et. al.*, followed in situ approach for synthesis of stable (Au NPs) / reduced graphene oxide hybrid materials using anti-oxidant rich ascorbic acid as reducing agent for both GO and Au ions and polyvinylpyrrolidone as stabilizing agent (54). Nile Blue A (NBA) was used as a probe molecule for surface-enhanced Raman spectroscopy (SERS) studies. Graphene acts as electron donor for Au NPs, whereas Nile Blue A acts as electron acceptor. Nano composites produced by this method exhibited fine tuneable surface decorated properties (54). Wang *et. al.*, prepared AuNP/L-cys/G composites for novel antibody immobilized HRP-labelled sandwiched electrochemical immunosensors for detecting human IgG (HIgG, Ag). SEM studies proved that graphene induces/controls the high surface area that leads to uniform growth of L-cys, which improved the anchoring ability of Au NPs and also increased high loading ability of biomolecules. These electrochemical immunosensors show precise detection limit up to 70 pg mL^{-1} and can act as convenient, low-cost effective, sensitive, and specialized materials for clinical applications (55).

Sharma *et. al.*, have chosen microwave irradiated technique for successful synthesis of Au NPs-reduced graphene oxide composites using ascorbic acid as an eco-friendly reducing agent (56). Well dispersed spherical shaped Au-NPs are produced by this technique with a size range of 2-20 nm (average particle size ~ 27nm) which was determined by small-angle X-ray scattering analysis (SAXS). The synthesized composite showed auspicious catalytical activity towards aerobic oxidation of benzyl alcohols to corresponding aldehydes. When compared to other composites such as Au/U_3O_8, Au/MgO, and Au-Pd/TiO_2, benzyl benzoate is the only by-product obtained by this process (56). Wang *et. al.*, preferred one-step solvothermal approach for depositing Au NPs on the surface of the graphene nanosheets (GNS) using ethylene glycol as the solvent and reducing agent. The synthesized Au NPs-GNS hybrids showed excellent electrochemical and electrocatalytic activity towards the oxidation of biomolecules such as ascorbic acid (AA), dopamine (DA), and uric acid (UA). These composite materials found their new application ability in manufacturing electrochemical sensors. The electrochemical activity depends upon high surface area and increased surface roughness due to deposition of Au NPs (57).

Pasricha *et. al.*, employed a novel green method for the simultaneous reduction of graphene oxide and NPs at room temperature using UV-assisted phosphotungstic acid (PTA). Phosphotungstic acid keep unique features such as 1) switched on and off reducing mechanism, 2) instantly reduces metal ions by electrolytically or photochemically, 3) stabilizes the NPs electrostatically and stereo chemically. Au/RGO, Ag/RGO and Pt/RGO sheets are prepared by this method. HRTEM analysis shows that this NPs exhibits different morphologies like Au-Spherical and Ag-dendritic structures. Microsecond electron transfer phenomenon detected by time-resolved photoluminescence spectroscopy (TRPL) demonstrates that these materials are worthy in optoelectronic applications (58). Zhang *et. al.*, have applied mild, fast, and facile one-pot photochemical synthetic method for preparing Ag NPs/RGO composites. Silver-ammonia complex [$Ag(NH_3)_2OH$] is used as precursor and stabilizing agent, photochemical reaction takes place by irradiating ammonia complex at 15 cm below a 450 W using medium pressure Hg lamp. Uniform dispersion of Ag NPs can be attained due to ammonia ligand which forms ligation with Ag NPs and controls the nucleation and growth of upcoming NPs. Ammonia ligand acts as scavenger for produced electrons and accelerate photo-excitation reactions, so the composites acts as super catalysts for reduction of 2-nitroaniline to 1,2-benzenediamine (59).

Wang *et. al.*, selected simple green and controllable method for synthesis of graphene/nano-Au composites by electrochemical co-reduction of graphene oxide and $HAuCl_4$ onto the glassy carbon electrode (GCE) by using cyclic voltammetry (60). The obtained composite hybrids showed remarkable electrocatalytic activity towards hydrogen peroxidase. Further these composites laid foundation for incorporation of enzymes like glucose oxidase, which acts as glucose biosensors for clinical applications due to low detection limit, high sensitivity, acceptable reproducibility, stability, selectivity and anti-interference ability. SEM analysis showed that GO appears as wrinkled and crumpled shape, whereas AuNPs/RGO showed curled shape. The electrochemical behaviour of composites increased due to synergic effect of graphene and large surface area of Au NPs (60). Liu *et. al.*, also followed a similar greener method for synthesis of Au NPs-reduced graphene oxide (AuNPs/RGO) composites films. By one-step coelectrodeposition of graphene-metal-composite films on glassy carbon electrode using cyclic voltammetry technique, the synthesized composites showed better catalytic activity towards biological molecules such as ascorbic acid (AA), dopamine (DA), and uric acid (UA) which coexists in biological systems. Herein the authors used ethylene glycol as stabilizing agent, these composites are stable even at high pH range (pH=11). From SEM and TEM analysis it is noted that these composites shows wrinkled texture (61).

Ag nanoparticles-reduced graphene oxide (Ag NPs/RGO) nanocomposites

Zhang *et. al.*, has demonstrated successfully a green, cost-effective, one-pot preparative route for synthesis of Ag NPs/RGOcomposites in aqueous solution using tannic acid (TA), an eco-friendly and water soluble polyphenol as mild reducing agent with redox potential -0.57 to -1.05V (at pH = 3.03-6.24). Composites show excellent surface enhanced Raman scattering (SERS) activity towards ρ-aminothiophenol (ρ –ATP) as SERS substrate, and also exhibit a notable catalytic performance towards the reduction of hydrogen peroxide. These composites is used in fabricating Glucose biosensors which is done by depositing immobilized glucose oxidase (GOD) enzyme into chitosan complexed Ag-NPs/RGO composites coated on a glassy carbon electrode and these electrodes has been tested for its real time applications such as sensing glucose detection in both buffer and human blood serum samples (62). Tang *et. al.*, have illustrated the green and efficient method for synthesis of Ag NPs decorated on graphene nanosheets using glucose as reducing agent (GSG) and poly (N-vinyl-2-pyrrolidone) (PVP) as surface modifier. The key point is that the oxygen functional groups present on the substrate influences its decoration with *in situ* formed Ag NPs. Based on this the author has synthesized two different substrates GSG-25 and GSG-40 by varying temperature conditions. The morphology of these substrates is examined by using TEM, and SERS analysis. Both analyses show positive impact towards GSG-25 substrate compared to GSG-40, because GSG-25 substrate carries more number of oxygen groups on it and hence it attracts more number of Ag NPs to be decorated, ultimately it leads to reduction of Rhodamine dye and shows enhanced catalytic activity (63). Li *et. al.*, elucidated green and facile approach for producing Ag NPs/RGO and Au NPs/RGO nanosheets using monosaccharide medicine glucosamine (GL) as reducing agent. Authors worked on different factors like 1) pH, 2) weight ratio of GL/GO and 3) temperature. The authors concluded that GL can extensively reduce GO under neutral pH conditions, the weight ratio is found to be 2.0: 1.0 and the optimal temperature is found to be 90°C. Thermo gravimetric (TGA) analysis results also stated that the mass loss of graphite was not observed up to 600°C, but the mass loss of GO was observed at 150°C and 250°C indicates the loss of oxygen functional groups takes place. An Au NPs/RGO composite shows catalytic activity towards Suzuki–Miyaura coupling reaction of phenyl halide and phenylboronic acid to produce biphenyl; Ag NPs/RGO shows activity towards SERS effect (64). Tian *et. al.*, portrayed eco-friendly, one pot synthesis of Ag NPs/RGO composites and their applications in photocurrent generation by using sodium hydroxide as reducing agent at 80°C. The hydroxyl groups present on graphene oxide acted as mild reducing agent for Ag^+ ions under basic condition. When sodium hydroxide was added to GO formation of Ag(OH) intermediate takes place which reduces Ag^+ ions to Ag^0 followed by nucleation of Ag NPs on the surface of GO simultaneously. Due to the presence of synergistic and surface Plasmon resonance properties in them Ag NPs/RGO composites shows positive photocurrent generation capacity compared to Ag NPs, GO and RGO tested individually (65). Sun *et. al.*, deliberated the existence of competitive surface-enhanced Raman scattering effects in noble metal NPs-decorated on graphene sheets (Au or Ag NPS/RGO) by taking three different probe molecules like rhodamine 6G, Nile blue A, and 4-aminobenzenethiol having their own coupling/binding abilities towards graphene sheets. Using sodium citrate as green reducing agent, SERS effects mainly originate by two possible sources such as electromagnetic and chemical mechanisms which further depend on surface Plasmon resonance and charge transfer factors. The authors studied these effects and came to conclusion that Nile blue A which shows strong SERS effect, rhodamine 6G shows moderate SERS effect and 4-aminobenzenethiol shows weak SERS effect. Among Au and Ag NPS, Ag NPs show high SERS effect than Au NP (66). Yuan *et. al.*, have demonstrated one-step facile method for green synthesis of graphene/Ag composites using sodium citrate as reducing and stabilizing agent, presence of surface Plasmon resonance property in them makes these Ag NPs to be evenly distributed on the RGO nanosheets. In addition, Ag NPs possess antibacterial activity; hence these can be used as potential graphene based biomaterials/disinfectants. TEM studies investigates that these Ag NPs has closely packed lamellar structure, the Ag crystallites are deposited on graphene surfaces acts as spacers to keep neighbouring sheets separate and shows curled and corrugated morphology. These composites show better antibacterial activity towards bacterial cultures such as *Coli bacillus and Canidia albicans* (67). Dinh *et. al.*, manufacture a fast, facile, low cost effective, large-scale productive and eco-friendly method for the preparation of dimensionally controlled highly conductive Ag NPs/RGO composite films by using vitamin C (ascorbic acid) as natural antioxidant and reducing agent. The authors noticed crumpled silk waves morphological Ag NPs decorated on RGO by maintaining sufficient sonication time period. These synthesized composite films showed wide scope of analytical applications such as catalysis, sensors and microchips (68). Yu *et. al.*, put a worthwhile effort for the preparation of graphene-Ag composites and their applications towards electrochemical detection of halide ions especially chloride ion using cyclic voltammetry. Through Raman studies it is cleared that large number of sp^3 hybridized carbon atoms in graphene oxide are transformed into sp^2 hybridized carbon atoms in reduced graphene oxide under the effect of ascorbic acid as reducing agent. Based on the oxidation-reduction potentials only the recognition/interaction ability of Ag and halide ions takes place. This composite exhibits good sensitivity and high reproducibility (69).

Liu *et. al.*, executed one-step microwave assisted rapid reduction method for the synthesis of Ag NPs/RGO composites using N, N-Dimethyl formamide (DMF) as solvent and reducing agent under irradiation with 750 W for 2min. DMF is decomposed into carbonyl and dimethylamine groups under high temperature, carbonyl group effectively reduces GO and $AgNO_3$ into Ag NPs/GN composite. Through XPS studies the authors concluded that 65% of the oxygen-containing functional groups can be successfully removed from the graphene oxide. TEM studies also determine that Ag NPs has been uniformly distributed on the surface of RGO sheets with more controllable diameter. These composites present notable catalytic activity towards hydrogen peroxidase reactions (70). Wang *et. al.*, assessed a simple one-pot hydrothermal method for producing Ag NPs with an average size of 12 nm and decorated on reduced graphene oxide using Gallic acid as reducing agent. TEM studies elaborate the morphology of GO to be flake-like shape with slight wrinkles on the surfaces indicating that RGO nanosheets are occupied with Ag NPs. XPS studies also confirmed that metallic Ag NPs are formed. The selective catalytical activity of these composites towards hydrogen peroxidase detection are tested using six biomolecules like dopamine, uric acid, glucose etc., which are chemically resemblance with each other with encouraging catalytic activity (71). Qin *et. al.*, have applied an easier, greener and safer method for synthesis of Ag NPs-reduced graphene oxide (Ag NPs/RGO) composites. They maintained strong alkaline conditions using NaOH as green reducing agent in one-pot hydrothermal technique. The synthesized composites showed active participation even at higher pH ranges around 6.5. They exhibit positive electrocatalytic activity towards hydrogen peroxide and anti-interference nature towards ascorbic acid (AA), dopamine (DA), uric acid (UA) and glucose. Electrocatalytic activity is compared with citrate-protected Ag NP-modified glassy carbon electrode (AgNP/GCE). These electrodes show long-term stability, reproducibility and repeatability (72).

Lin-Jun *et. al.*, used solvothermal technique as their greener tool for synthesis of Ag NPs-reduced graphene oxide (Ag NP/RGO) composites using ethylene glycol as reducing agent. The composites highlight higher dispersibility and electroconductibility. The electro conductibility nature is mainly due to synergistic effect between graphene sheet and deposited Ag NPs (73).

Pd nanoparticles-reduced graphene oxide (PdNPs/RGO) nanocomposites

Zhang *et. al.*, have chosen microwave-assisted one-pot preparative and also a greener method as a superior pathway for synthesis of Pd NPs/RGO composites using tannic acid as reducing agent. These Pd NPs morphology depends on loading capacity and microwave irradiation time. This composite shows better electrocatalytic activity towards methanol electrooxidation in alkali medium. When compared to commercially available Pd/C catalyst, these composites acts as anodic catalyst and has wide scope of

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applications in direct methanol fuel cell technology (DMFC) as high efficiency, low pollution emitter power source generating materials for fuel-cell vehicles (74). Jiang *et. al.*, has unrivalled the facile electrochemical codeposition approach for obtaining clean graphene-Pd nanocomposites which acts as anode catalyst for formic acid oxidation (FAO). The process is called clean because it is a reductant and surfactant free synthesis. Nowadays the Pd-based catalysts are gaining much more importance due to its lower cost, higher resistance towards carbon monoxide (CO) in comparison to Pt-catalysts which causes poisoning of catalyst. Electrochemically reduced graphene oxide and Pd nanocomposites (ERGO-Pd) exhibit 5 times higher catalytic activity and better stability towards (FAO) compared to Pd/C catalyst by using cyclic voltammetry, these composites further can be used as electrochemical sensors and electrocatalysis materials (75).

Ir nanoparticles - reduced graphene oxide (Ir NPs/RGO) nanocomposites

Shim *et. al.*, has taken strenuous effort in synthesis of decorated Iridium NPs on polyvinylpyrrolidone functionalized reduced graphene oxide (Ir NPs/pRGO) composites using ethylene glycol as solvent and as well as green reducing agent. Herein the basic point lied in this process is Iridium NPs which exists in Ir(0) oxidation state only shows active electrocatalytic activity towards oxygen reduction reactions (ORR) and proton-exchange membrane fuel cells (PEMFC). Other than this Iridium NPs which can exist in any other forms are electrocatalytically inactive. Ir NPs are corrosion-resistive, high stability even in acidic conditions. SEM, TEM and HRTEM analysis of these composites states that these exhibit crystalline morphology. The electrocatalytic activity is measured by rotating disk electrode voltammetry (RDE) and cyclic voltammetry (CV). Comparison was done by using pRGO-H_2, pRGO-O_2, and commercially available Ir-20/C catalysts (76).

Pt nanoparticles - reduced graphene oxide (PtNPs/RGO) nanocomposites

Kim *et. al.*, has conceived the beautiful technique for one-pot synthesis of aqueous dispersible graphene platinum nanohybrids using vitamin C as reducing agent. They exhibit face-centered cubic (FCC) crystalinity nature in them. These Nano hybrids are further coated as thin films by using electro-spray method at room temperature which acts as counter electrodes (CEs) for dye-sensitized solar cells (DSSCs) and the electrocatalytic activity of these materials for redox couple reactions are measured using cyclic voltammetry (CV) and electrochemical impedance spectroscopy. The interfacial charge transfer property was compared with graphene nanosheet counter electrodes and platinum doped graphene Nano hybrids. The charge transfer activity is noticed obviously high for nanohybrids (77). Qian *et. al.*, flourished their task by synthesizing Pt NPs-reduced graphene oxide (PtNPs/RGO) composites. In which Pt NPs shows uniform particle nature and distribution property, using sodium citrate as novel and greener approach as reducing and stabilizing agent. SEM studies explores some of the facts that the reduced graphene oxide nanosheets are thinner (1nm), transparent and wrinkled in looking. HRTEM of Pt NPs shows that these exist as single crystals. The electrochemical activity of these composites are tested by selecting ferrocyanide system $Fe(CN)_6^{3-/4-}$ as redox probe molecule and the activity is compared with graphene nanosheets (GNS) and (Pt NPs/RGO) composites coated separately on glassy carbon electrode (GCE) using cyclic voltammetry as measurement tool. The electrochemical activity is getting lowered in acidic conditions (78). Vinayan *et. al.*, has performed a riveting research and leads to invention of two novel greener methods in which utilizing of natural resources like solar radiation and hydrogen gas as reducing agents for synthesis of Pt NPs-reduced graphene oxide (Pt NPs/RGO) composites, they followed an in situ method because the process is low cost, energy effective, large scale production, less effort, fast, and give uniform distribution of Pt NPs on graphene sheets with optimum particle size. These composites acted as cathode material and showed electrocatalytic activity towards proton exchange membrane fuel cell technology (PEMFC) and also effective for oxygen reduction reactions (ORR). Electrocatalytic activity is measured by using cyclic voltammetry and compared with commercially available Pt-C catalysts. XPS studies gives information that these Pt NPs exists in +4 and +2 oxidation states. TGA data states that these materials undergo decomposition at above 525˚C, SEM and TEM analysis tells that these sheets exhibit wrinkled morphology, XRD analysis defines that these Pt NPs possess crystalline nature (79).

Liu *et. al.*, has demonstrated the importance of synthesis of Pt NPs on reduced graphene oxide (Pt NPs/EGS) composites by using microwave-assisted technique. The author has noticed that this process is polymer free, *in situ* reduction route, simple, rapid and effective method. Using ethylene glycol as green reducing agent, the synthesized composites exhibit good catalytic activity towards methanol oxidation. And the Pt based materials also pays an applicable applications in various fields such as fuel dells, sensors, petroleum, automotive industries. Raman spectroscopic techniques confirms that the hexagonally packed network of carbon atoms are attained by this technique and TEM studies explains that the Pt NPs acquires crystalline nature (80). Ullah *et. al.*, has developed a noteworthy process which is fast, facile, one-pot synthesis of Pt NPs- reduced graphene oxide (PtNPs/RGO) composites using microwave assisted technique as greener approach. These composites act as photocatalyst for high efficient decomposition of organic pollutants/dyes such as rhodamine B (RhB) and Methylene blue (MB) used as standard model dyes. Herein the authors prepared five different (Pt NPs/RGO) composites and investigated for their high catalytic nature. XRD analysis states that these composites exhibits face–centered-cubic-phase. SEM and TEM analysis reports that graphene sheets appears as flaky texture acting as bridging substance for Pt NPs and transfer of photo generated electrons. Among all the composites Pt/G3 material shows more photocatalytic nature because the homogenous distribution of Pt NPs on graphene sheets was observed. These composites further are applied as semiconductor, electron collector, and transport materials (81). Guo *et. al.*, have demonstrated conspicuous method for the preparation of Pt NPs ensemble-on-graphene hybrid nanosheet (PNPEGHNs) composites. These composites show electrocatalytic activity towards hydrogen peroxide, trinitrotoluene, neurotransmitters (DA), and acetaminophen which they act as organic and inorganic electro active species, here in the authors employed one-step microwave-assisted route due to presence of more beneficial properties such as high conductivity, small size, good uniform size distribution, and controllable high-metal-loading level on graphene sheets. Ethylene glycol (EG) was used as reducing agent and poly (methacrylic acid sodium salt) (PMAA) as linker or protecting agent. The electrocatalytic activity towards trinitrotoluene was studied exclusively by using adsorptive stripping voltammetry (ASV). The electrocatalytic nature of these composites is compared with graphene glassy carbon electrode (G/GCE). These composites further are applied as bio-sensing, energy conversion and electronic systems (82). Wu *et. al.*, has breakthrough a facile hydrothermal technique as a greener and safer method for synthesis of clean Pt NPs-reduced graphene oxide (Pt NPs/RGO) composites. Authors have noticed that the spontaneous reduction of $PtCl_4^{2-}$ and graphene oxide (GO) take place, where KOH acts as aqueous reducing medium, Due to the presence of synergistic effect between Pt NPs and RGO these composites Pt NPs/RGO expresses higher catalytic activity and better tolerance nature towards methanol oxidation, when compared to Pt/C catalyst. XPS results suggest that KOH plays a vital role in transformation of graphene oxide (GO) to reduced graphene oxide (RGO). Electrocatalytic activity of Pt NPs/RGO can be increased by altering the pH conditions and the best suited is (pH= 7), these composites can be used as sensors fuel cells and catalyst supports (83).

Liu *et. al.*, has instigated the method for synthesis of nanocomposite films of Pt NPs deposited on expandable graphene sheets (P NPst/EGS) fabricated on conductive indium tin oxide glass electrodes using electrochemical deposition method and also a greener method where KCl solution is used as *in situ* electrochemical reducing agent for reduction of expandable graphene oxide (EGO) to expandable graphene nano sheets (EGS). FE-SEM analysis states higher carbon: oxygen ratio in (EGS) films compared to (EGO) and elecrocatalytic activity and stability of these composites towards methanol oxidation are measured using cyclic voltammetry and chronoamperometry (84). Zhou *et. al.*, has fostered the development of one-step electrochemical greener approach for synthesis of highly dispersed Pt NPs on reduced graphene oxide (Pt NPs/RGO) nanocomposites. With uniform particle nature of 10 nm it exhibits higher electrocatalytic activity and long-term stability towards methanol electro-oxidation measured by cyclic voltammetry and chronoamperometry and this result was compared with Pt NPs graphene glassy carbon electrode (PtNPsG/GCE) and Pt NPs graphene Vulcan glassy carbon electrode (PtNPsG/Vulcan GCE). The interesting results found here are the (PtNPsG/GCE) exhibits 3 times electrochemical activity and 14 times higher stability compared to (PtNPsG/Vulcan GCE) (85). Wu *et. al.*, depicted their work successfully for functionalization of graphene sheets (FGS) with chitosan, decorating these sheets with Pt NPs using potentiostatic electrodeposition method and immobilization of glucose oxidase (GOD) enzyme to form (GOD/Pt/FGS/chitosan) bionano omposite film for glucose sensing material in human plasma samples. The presence of synergy effect between FGS and Pt NPs towards hydrogen peroxide leads to biosensors. Biosensors possess good reproducibility, long-term stability, shows negligible interfering response towards ascorbic acid and uric acid. TEM analytical studies have determined that these FGSs exist as wrinkled in nature and it is helpful in maintaining high surface area. Cyclic voltammetry experiments prove that when the reduction current increases potential decreases due to electrocatalytic activity of Pt NPs and graphene. The sensing activity is tested by comparing Pt NP/FGSs versus Pt/Pb alloy, and NP/carbon nano-tube based sensors (86). Xu *et. al.*, introduced the easiest method for synthesis of Pt NPs-reduced graphene oxide (Pt NPs/RGO) composites for nonenzymatic detection of hydrogen peroxide using photochemical reduction as convenient, clean, and greener method. The precursors utilized here are potassium tetrachloroplatinate, graphene oxide and polyvinylpyrrolidone as stabilizing agent. AFM results suggest that the thickness of the graphene sheet was increased due to attachment of Pt NPs. Electrocatalytic activities of these composites are investigated by fabricating two types of electrode materials such as Pt NPs-RGO-glassy carbon electrode (PtNPs/RGO/GCE) and platinum-glassy carbon electrode (Pt/GCE) for comparison study. Herein the graphene matrix acts as supportive and dispersive material for Pt NPs that helps in building high surface area and catalytic activity (87).

Applications of reduced graphene oxide noble metal composites

From discussion in the previous sections it is clear that graphene is combined with noble metals such as Au, Ag, Pt, Pd, Ir, etc, by various greener approaches or techniques. The graphene-noble metal nanocomposites not only preserve the favourable properties of graphene and metal, but also greatly enhance the intrinsic properties of the composites such as existence of synergetic effect that present between the graphene sheets and noble metals. The improved performance of graphene-noble metal nanocomposites is utilized in various applications such as catalysis, energy storage and conversion, and sensors.

Catalysis

Carbon materials have been widely used as a supporting material for immobilization of inorganic catalysts due to large specific surface area, excellent thermal and electrical conductivity, low cost effective and high chemical inertness, easy modification and high reusability nature. Like other carbon catalysts these synthesized graphene-noble metal composites show catalytic activity towards chemical, electrochemical as well as in photochemical reactions.

Catalysis in c-c coupling reactions

As the graphene-noble metal nanocomposite materials exhibit large specific surface area, these composites can be better applied as catalysts in Heck reaction (88, 89) and Suzuki coupling reaction (90, 91) in which C-C coupling occurs. The rate of these reactions is far better when platinum based graphene composites are used as catalytic materials (Pt NPs/RGO). These reactions can also be preceded by applying other graphene-noble metal composites such as Au and Ag but the rate of these reactions is slower compared to Pt based nanocomposites.

Electrocatalysis

Graphene-noble metal composites show immense electrocatalytic activity towards some electrochemical reactions such as methanol oxidation reactions (MOR), oxygen reduction reaction (ORR) and proton exchange membrane fuel cell technology (PEMFC). The graphene sheets with high surface area and high dispersive nature act as catalyst. Also, its high conductivity ability of acceleration of the charge transfer property enhances the rate of reactions. Normally, Pt and Pd based nanomaterials are best suited for this work.

Energy conversion and storage devices

Due to the increase in demand for energy reproducing systems in recent times and also to decrease the air pollution and global warming effects of environment, many efforts have been put forward for the designing of energy storage/conversion devices with high power and energy densities. These graphene-noble metal composites possess many advantageous properties such as high electrical and thermal conductivity, huge surface area, excellent mechanical strength and high chemical stability brought/design these materials as supercapacitors (92), lithium ion batteries (93), solar cells and fuel cells (94).

Sensors

The graphene-noble metal composites have been recently entered into the analytical science and play a pivotal role in performing novel functions such as gas sensing and also act as biosensors in biosensing of biomolecules such as hydrogen peroxide, glucose, dopamine, uric acid, pesticides etc. These composites consist of materials with high surface area which makes them to lose electron during the application of sensing probes.

CONCLUSION

In summary, graphene nanosheets have been decorated with various noble metals such as Au, Ag, Pt and Pd to form nanocomposites. Diverse approaches and techniques have been carried out to prepare graphene noble metal composites using natural reducing agents, microwave assisted, solvothermal, hydrothermal, UV, photochemical and electrochemical methods. These nanocomposites exhibit excellent properties and improved functionalities due to the presence of synergetic effect present between graphene nanosheets and noble metal nanoparticles which make these materials to be applicable in various fields such as catalysis, energy storage devices, and analytical sciences like sensing applications. The catalytic application of these nanocomposites is considered to be as significant application because it forms a foundation for developing many other applications of graphene-noble metal composites such as electrocatalysis in developing electrochemical sensors, fuel cells, photo catalysis in hydrogen energy and solar cells. The major task that left behind the application of these composites is to

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develop the high capacity energy storage systems to keep the environment cleaner and safer. More efforts are needed for the preparation of graphene-noble metal composites to apply as potential materials in novel applications. The first task is to prepare the graphene nanosheets with desirable or controllable shape, size, with low cost and low defects and to produce in eco-friendly manner. The second task is to control the size, morphology, crystallinity, phase composition distribution of these second components namely noble metal nanoparticles on graphene sheets. The properties and functions of these components mainly depend on second components only. However, the precise mechanism for attachment of these noble metals with graphene sheets are not studied well and hence thorough investigation would be performed for development of better nanocomposites. It is noticed that very little amount of work has been carried out to synthesise graphene-noble metal composites using green reducing techniques or approaches. Hence future researchers will have to put their efforts in improving this area of synthesis as well as their applications in novel areas. Finally, the development and successful implementation of these graphene-noble metal nanocomposites for novel applications require interdisciplinary research involving chemistry, biology, electronics, physics and material sciences.

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